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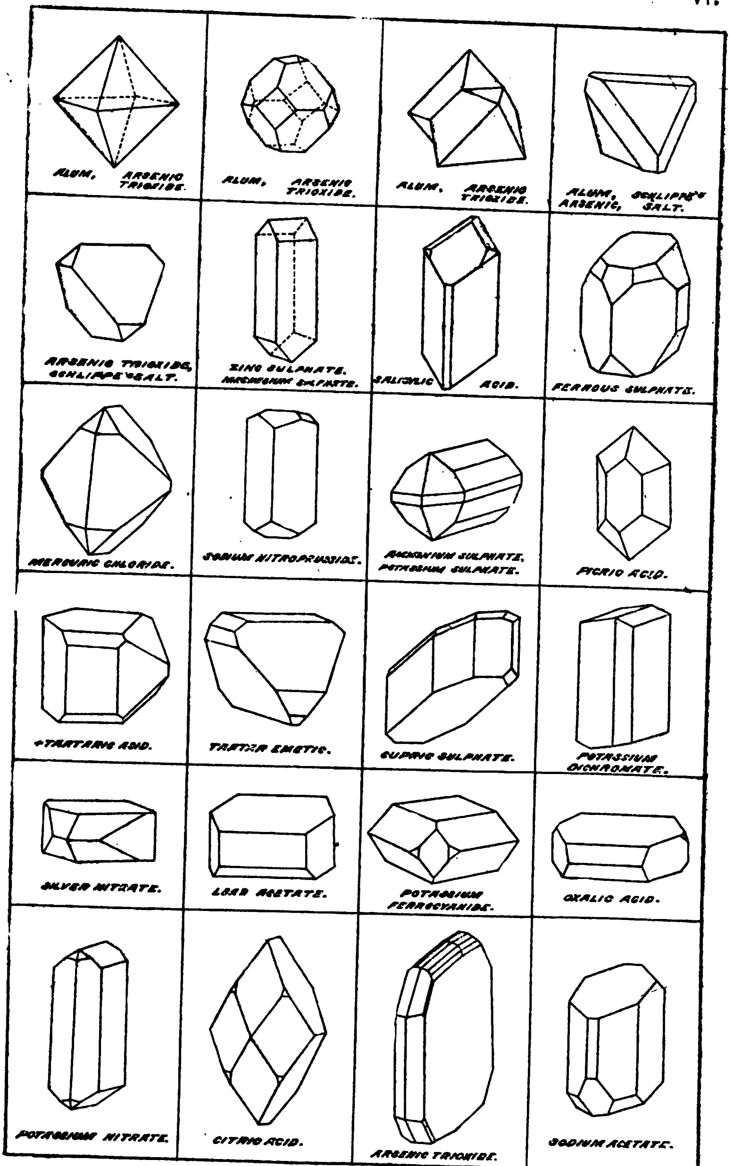
from the author



Charlotte S. Curtman, Del.

USES, TESTS FOR PURITY AND PREPARATION

—OF—

CHEMICAL REAGENTS,

EMPLOYED IN

QUALITATIVE, QUANTITATIVE, VOLUMETRIC, DOCIMASTIC, MICROSCOPIC AND PETROGRAPHIC ANALYSIS,

WITH A SUPPLEMENT ON THE USE OF

THE SPECTROSCOPE.

BY

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WITH TWELVE PLATES.

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PREFACE.

Having for a number of years been engaged in a variety of analytical work, the author has often experienced difficulty in readily obtaining some of the rarer reagents, or in procuring those which were obtainable in the market, of the necessary degree of purity. This experience has undoubtedly been shared by most practical analysts, and cases of misplaced confidence in "chemically pure" reagents have neither been few nor far between.

So far as the reagents in common use are concerned, there certainly has, in late years, been a great improvement, but even now it is very difficult to procure, e. g., concentrated sulphuric acid completely free from arsenic and from "nitrose," and absolutely pure zinc is very precious, indeed. The practice of testing the reagents is as necessary as ever in order to obtain reliable results, and a neglect of this precaution in forensic cases would be criminal. In the manuals of analytical chemistry modes of testing the purity of all reagents in common use are fully described, but to find a description of the great number of new reagents introduced recently into special classes of work, we have to resort to journals and monographs, and the information is scattered throughout the literature of the day. Even the valuable pamphlet of Dr. Krauch, chemist of E. Merck's celebrated establishment, which appeared late in 1888, contains only 116 headings.

The difficulty of obtaining the desired information at the moment of need having been brought home time and again, the author was prompted to undertake the laborious task of compiling all the information to be found in the literature accessible to him, and the result is before the reader. The manuscript was nearly completed and publication begun in May, 1888, as a serial in the *Druggist*, a monthly issued by the Meyer Brothers Drug Co. As but few pages appeared in each number, the completion of the printing was considerably delayed. To collect the 400 different items treated in book form, electrotype plates were made as each number of the journal appeared, and this necessitated the deferring of any corrections or omissions to a supplement.

Whenever practicable, the author has endeavored to give proper credit to originators of analytical processes, and any omis-

sions which may have occurred are certainly not intentional. Out of the vast amount of material before him he has selected what appeared to him most important, and in regard to critical sifting he has spared no effort. Many of the new reactions were thoroughly tested before admitting them, and hundreds of experiments were made to verify statements in regard to the reliability of new methods.

There being only metric weights and measures referred to in the volume, and therefore no possible chance of a mistake, the author may perhaps be pardoned the liberty of abbreviating gramme by gr.

As the spectroscope forms so valuable an adjunct to the means of analytical research, a short chapter has been added, describing the use of the simpler and inexpensive forms usually employed in the laboratory, with the aid of the accessories everywhere at hand. The descriptions of the spectra give the position of lines and bands accurately by wavelengths, so that they may be conveniently mapped out on diagrams. A number of plates illustrate the text and afford aid in the identification of the spectra. As only a limited number could find a place in the short chapter, the author has selected of the emission spectra such as may be easily produced by the aid of a Bunsen gas burner, or a strong alcohol lamp, and of absorption spectra those of the coloring constituents of blood and such materials as might be most easily mistaken for them, some others referring to the detection of adulteration of red wine, or illustrating chemical reactions (e. g. furfurol-urea) or identifying color reagents used as indicators in volumetric work.

The author hopes that his colleagues of the craft may find his little volume of some use to them, and that they will pass a lenient judgment on its short-comings.

CHAS. O. CURTMAN.

ST. LOUIS, MO., March, 1890.

INTRODUCTION.

In the succeeding pages the attempt is made to describe the reagents used in the various processes of analysis.

The name *reagent* might be applied to all bodies, simple or compound, which, when brought together with others, produce, by their mutual action upon each other, a change of condition in color, odor, state of aggregation, temperature, etc., etc. It is, however, usually restricted to those chemicals which we employ for the purpose of eliciting information as to the constituents of bodies, whose composition we desire to ascertain. The change produced by the action of the bodies brought together is called a *reaction*, and is due to a rearrangement of their atoms into new molecules. When a certain substance effects such a change only in one other, we call it a *special reagent* for that substance ; when it produces a similar effect upon a larger number, it is called a *group-reagent* or *general reagent;* and as the effect is due to the mutual action upon each other, each of the substances may be regarded as the reagent for the other.

The book is not intended to be a guide to analysis or to compete in any way with standard works on that subject, but rather to serve as a supplement to them, to aid the analyst in selecting, testing and preparing the reagents he needs, and to gather into a single volume information now scattered over a vast extent of chemical literature.

The arrangement adopted is in most cases to give, first, the USE of the reagent; next, TESTS for its purity, and, lastly, such methods of PREPARATION as are suitable for making smaller quantities for use in the laboratory.

In describing the USE of reagents the aim has been to give only a brief mention of the manifold applications of general reagents, and to allude but shortly to the well-known analytical methods and conditions under which reactions occur, or the apparatus used, while in the case of those less familiarly known, and used only in special processes, *reactions*, as well as *reagents*, have been described. Space has been given even to some whose use might have been deemed superfluous, as they may occasionally prove useful under special conditions.

The enumeration of TESTS for purity includes, in most cases, a short description of physical properties, which are often valuable helps to identification. Thus, the *crystalline form*, *melting* and *boiling points*, *specific gravity*, *solubility* at different temperatures in water and in other solvents is described. On the other hand, such self-evident tests for identity as are to prove that magnesium sulphate really contains magnesium and sulphuric acid are generally omitted, and only those tests mentioned which are to prove freedom from impurities. It is hardly necessary to observe that for many purposes *absolutely pure reagents* are not required, that only the absence of certain kinds of impurities may be needed to render the reagents serviceable, and that it would entail needless trouble and expense to employ pure articles where ordinary commercial ones suffice. In most cases the tests for absence of all impurities are given and from them only those need to be selected which are essential for the special purpose.

The description of PREPARATION in some cases confines itself to modes of purification of commercial articles; in others it gives a full outline of the manufacture from the crude material.

For greater ease of controlling quantitative relations, making volumetric solutions, etc., the molecular weights are given with most articles, the calculations being based on the table of atomic weights on adjoining page. Wherever water, alcohol or acids are mentioned without special qualifications, the pure substances, of the strength stated in the description of these agents, are intended. Thermometric degrees refer to centigrade, boiling points, etc., to normal conditions of 760 millimetres pressure.

The arrangement of the different articles is according to the alphabetical sequence of the groups, in which the different members again follow in alphabetical order. Thus, the first group, *acids*, gives in detail acetic, boric, chromic, etc. The many *color reagents and indicators* used and proposed, mostly for volumetric processes, have been united into a chapter, the individuals of which are arranged in alphabetical detail. A general index and another giving under the name of each substance the tests described for its detection is added at the end of the volume.

Table of Atomic Weights. H=1. Periodic System of Elements.

I. MONADS.	II. DYADS.	III. TRIADS.	IV. TETRADS.	V. TRIADS and PENTADS.	VI. DYADS and HEXADS.	VII. MONADS and HEPTADS.	VIII.
Li=7.007	Be=9.085	B=10.941	C=11.974	N=14.021	O=15.96	F=18.984	
Na=22.998	Mg=23.959	Al=27.003	Si=28.195	P=30.958	S=31.984	Cl=35.37	Fe=55.913 Ni=57.928 Co=58.887 Cu=63.173
K=39.019	Ca=39.99	Sc=43.98	Ti=48. . .	Vd=51.256	Cr=52.009	Mn=53.906	
(Cu=63.173)	Zn=64.905	Ga=68.854	Ge=72.28	As=74.918	Se=78.797	Br=79.768	Ru=101 5 Rh=104.055 Pd=105.737 Ag=107.675
Rb=85.251	Sr=87.374	Yt=89.816	Zr=89.367	Nb=94	Mo=95.888	—	
(Ag=107.675)	Cd=111.77	In=113.398	Sn=117.698	Sb=119.955	Te=125. . .	I=126.557	
Cs=132.583	Ba=136.763	La=138.526	Ce=140.424	Di=146.18	Tb=148.8 (?)	—	
—	—	—	—	Er=165.891	—	—	Os=191.12 Ir=192.651 Pt=194.415 Au=196.155
—	—	Yb=172.76	—	Ta=182.144	W=183.61	—	
(Au=196.155)	Hg=199.712	Tl=203.715	Pb=206.471	Bi=207.523	Ng=214	—	
—	—	—	Th=233.414	—	Ur=238.482	—	

MULTIPLES OF SOME ATOMIC WEIGHTS IN FREQUENT USE.

H	1	2	3	4	5	6	7	8	9
O	15.96	31.92	47.88	63.84	79.80	95.76	111.72	127.68	143.64
H_2O	17.96	35.92	53.88	71.84	89.80	107.76	125.72	143.68	161.64
N	14.021	28.042	42.063	56.084	70 105	84.126	98.147	112.168	126.189
NH_4	18.021	36.042	54.063	72.084	90.105	108.126	126.147	144.168	162.189
NO_3	61.901	123.802	185.703	247.604	309.505	371.406	433.307	495.208	557.109
C	11.974	23.948	35.922	47.896	59.870	71.844	83.818	95.792	107.766
CO_3	59.854	119.708	179.562	239.416	299.270	359.124	418.978	478 832	538.686
Cl	35.37	70.74	106.11	141.48	176.85	212.22	247.59	282.96	318.33
Br	79.768	159.536	239.304	319.072	398.840	478.608	558.376	638.144	717.912
I	126.557	253.114	379.671	506.228	632.785	759.342	885.899	1012.456	1139.013
S	31.984	63.968	95.952	127.936	159.920	191.904	223.888	255.872	287.856
SO_4	95.824	191.648	287.472	383.296	479.120	574.944	670.768	766.592	862.416
PO_4	94.798	189.596	284.394	379.192	473.990	568.788	663.586	758.384	853.182
K	39.019	78.038	117.057	156.076	195.095	234.114	273.233	312.252	351.171
Na	22.998	45.996	68.994	91.992	114.990	137.988	160.986	183.984	206.982

ACIDS.

ACETIC ACID, $H C_2 H_3 O_2$.

USES. To separate calcium oxalate from phosphate, barium chromate from strontium chromate, zinc sulphide from manganese and other sulphides, to acidulate solutions, etc.

U. S. P. acid has specific gravity 1.048, and contains thirty-six per cent of absolute acid. It is generally sold of sufficient purity for analysis.

TESTS. It should leave no residue on evaporation (absence of non-volatile matters).

No precipitate should be produced by barium chloride (absence of sulphates), nor by silver nitrate (absence of chlorides), nor with ammonium oxalate (absence of calcium salts).

No precipitate should be produced by hydrogen sulphide (absence of arsenic and copper groups), nor, after neutralization with ammonium hydrate, by ammonium sulphide (absence of iron and aluminium groups).

No bleaching of indigo should occur on heating (absence of nitric acid). After neutralization by sodium carbonate, no empyreumatic odor nor bleaching of dilute potassium permanganate solution should indicate organic impurities.

PURIFICATION of impure acid may be accomplished by digesting it with some potassium permanganate, then adding sodium acetate and distilling.

BORIC OR BORACIC ACID, $H_3 B O_3$.

USED occasionally instead of borax in assaying and in blow-pipe analysis; also to liberate volatile acids, etc.; also in the preparation of ammonium borofluoride, a reagent for potassium.

TESTS. The colorless, transparent, scaly crystals dissolve without residue in 26 parts of cold, 3 parts of boiling water, and in 15 parts of cold alcohol. The watery solution, acidulated with nitric acid, should not be precipitated by barium chloride or silver nitrate, nor be colored red by potassium sulpho cyanide. When mixed with strong sulphuric acid, a crystal of ferrous sulphate should not produce a brown, nor a few drops of di-phenylamine a blue color (absence of nitrates). Hydrogen sulphide should produce neither color nor precipitate in the watery solution, either before or after

addition of ammonia to alkaline reaction. Heated on platinum foil, the acid should readily fuse into a glassy, transparent mass.

PREPARATION. Pure borax is dissolved in twice its weight of pure boiling water, one-half its weight of very concentrated hydrochloric acid is thoroughly mixed with it, and the liquid set aside to cool and crystallize. The crystals are drained on a funnel, washed with a little very cold, pure water, then redissolved in 5 parts of boiling water, and the purified crystals are drained and dried.

CHROMIC ACID ANHYDRIDE, $Cr\,O_3$.

USES. Chromic acid is a strong oxidizing agent, but is seldom employed in the pure state. A very weak solution in dilute glycerin serves to harden tissues for microscopical examination. It is also used to produce with strychnia the characteristic color reactions; to convert alcohol into aldehyde, etc.

TESTS. The commercial article is of sufficient purity, forming long, scarlet, rhombic crystals.

PREPARATION. Dissolve, by means of heat, two parts of potassium dichromate in a mixture of seven parts of concentrated sulphuric acid and five parts of water, set aside until the crystals of potassium sulphate have separated; pour off the red liquid; add eight more parts of concentrated sulphuric acid, and finally drain the crystals of chromic acid on a funnel closed with an asbestos plug. For most uses potassium dichromate mixed with sulphuric acid will answer all purposes, without separating the acid.

CITRIC ACID, $H_3\,C_6\,H_5\,O_7 + H_2\,O$.

USES. Citric acid is occasionally employed instead of acetic acid for acidulation in urine analysis, also in the determination of phosphoric acid.

TESTS. The colorless transparent rhombic crystals should leave no residue on ignition upon platinum foil. It should dissolve in three-fourths of its weight of cool water and in one-half of its weight of boiling water. At 15° C., one part should dissolve in 1.15 parts of 80% alcohol. 0.7 grammes of citric acid should accurately saturate 10 Cc. of normal potassium hydrate solution, phenol phthalein being used as indicator.

GALLIC ACID, $H\,C_7\,H_5\,O_5$.

USES. To show the presence of ferrous salts in mineral waters, etc., also to indicate the presence of *free* mineral acids (*Flueckiger*). For this purpose, three parts of ferrous sulphate and two parts of gallic acid are each dissolved in 100 parts of water and then mixed. To this colorless mixture one part of sodium acetate is added, which

produces a violet color. When a small quantity of this freshly prepared mixture is dropped into a liquid containing free mineral acids the color is discharged.

HYDRIODIC ACID, H I.

USES. It serves to recognize some oxygenized ethereal oils, which unite with the gaseous acid and may then, by heating with alcoholic soda solution, be converted into terpenes. A concentrated aqueous solution is used in blow-pipe analysis.

TESTS. The commercial liquid acid is suitable for blow-pipe work, even when it has turned brown from partial decomposition. The gas for oil analysis must be prepared when needed.

PREPARATION. Into a tubulated retort of 500 Cc. capacity place 100 Cc. heavy paraffin oil, then 10 grammes white phosphorus ; add carefully and gradually 128.2 grammes powdered iodine, and lastly, 18 Cc. pure water, drop by drop. Heat gently and dry the gas by passing over anhydrous phosphoric acid.

HYDROBROMIC ACID, H Br.

USES. Concentrated, pure hydrobromic acid has been recently employed as a solvent for mercury, lead and copper, also for lead sulphate and especially for metallic sulphides. In conjunction with copper amalgam, it converts sulphur, either free or in sulphides, into hydrogen sulphide, which may be accurately determined by absorption. It is also employed as a delicate test for copper.

TESTS. No residue should be left on evaporation. Barium chloride must give no precipitate. On addition of chlorine water chloroform shaken up with it should not show the iodine color. The precipitate with silver nitrate should be almost insoluble in aqua ammonia of U. S. P. strength, and in the ammoniacal filtrate, nitric acid should cause only a slight turbidity.

PREPARATION. Hydrobromic acid of great concentration and purity is best made by *Harding's* method. The vapor of bromine is first passed over red hot manganese dioxide to destroy organic impurities, then, together with pure hydrogen gas, is passed through a tube of platinum containing a layer of finely divided metallic platinum (platinized asbestos) heated to a bright red heat. The elements unite and the gaseous hydrobromic acid is passed first through a tube containing antimony, to absorb free bromine, then through a wash bottle, and is finally received into a cool receiver containing distilled water.

Or (according to Squibb) seven parts of pure concentrated sulphuric acid are added to one part of pure water, and, after cooling, are slowly poured, with constant stirring, into a hot solution

of six parts of pure potassium bromide in six parts of pure water. The mixture is set aside for twenty-four hours, the liquid is decanted from the crystals of potassium sulphate, transferred to a retort and distilled.

Acid of sufficient purity is now sold by dealers.

Hydrochloric Acid, H Cl.

USED as a general solvent; also to detect lead, silver, mercurous salts and free ammonia, to acidulate, to liberate boracic and other acids.

TESTS. Colorless liquid leaving no residue on evaporation.

Must not color a mixture of starch and potassium iodide (absence of chlorine and of ferric chloride).

Must not bleach blue iodized starch in dilution (absence of sulphurous acid).

No precipitate should be produced by barium chloride (absence of sulphates), nor by hydrogen sulphide (absence of arsenic and copper groups and sulphurous acid), nor, after neutralizing with ammonia, by ammonium sulphide (absence of iron and aluminium groups).

It should leave chloroform colorless, even after addition of chlorine water (absence of iodine, bromine).

When hydrochloric acid is to be used for arsenic testing, its perfect freedom from even traces of arsenic must be proven by placing about 2Cc of the acid, diluted with an equal amount of water, into a test tube, adding a little pure granulated zinc, and covering the mouth of the test tube with a piece of filter paper, moistened with a drop of silver nitrate solution; or inserting a slip of the paper with the silver solution into a slit of a loosely fitting cork, so as to hang into the test tube without coming in contact with its sides.

Hydrogen gas will be evolved, which, if arsenic be present, will contain arsenetted hydrogen and blacken the silver spot on the paper. If sulphur dioxide be present, blackening will also occur through its reduction and formation of hydrogen sulphide. A paper moistened with lead acetate will be blackened by sulphur, but not by arsenic.

To *purify* crude hydrochloric acid, which generally contains arsenic, one litre of it is mixed with 10Cc. of concentrated stannous chloride solution (or four grammes of finely granulated tin), and permitted to stand for twenty-four hours, after which time a few drops of the clear acid must show a slight excess of stannous chloride, by producing a precipitate in a solution of mercuric chloride. The acid is then separated from the precipitate, placed

into a retort and, after adding twenty-five grammes of sodium chloride, distilled into a receiver containing 500Cc. of pure water, until most of the acid has passed over. As perfectly pure acid may be obtained cheaply and readily, it will rarely be advantageous to purify the crude on a small scale.

Hydrochloric acid of U. S. P. strength has specific gravity 1.16, contains 31.9 per centof HCl, and is suitable for analytical purposes.

For volumetric analysis, *normal hydrochloric acid*, containing 36.37 grammes of HCl in one litre, is made by diluting the strong acid carefully until it accurately neutralizes an equal volume of normal alkali solution.

A most accurate standard solution, by which the whole series of normal alkali and acid solutions may be adjusted, is obtained by titration with deci-normal solution of silver nitrate.

HYDROFLUORIC ACID, H F.

USED to decompose minerals containing borates and silicates either in form of gas or in watery solution.

TESTS. Liquid hydrofluoric acid, as supplied by dealers in gutta percha bottles, is generally pure, but if made from impure fluorspar may contain hydro-fluo-silicic acid, and should, therefore, be tested by evaporation on platinum foil, when no residue should be left; also by saturation with pure potassium hydrate, when it should yield no precipitate of potassium silico fluoride.

PREPARATION. As the apparatus for making the liquid acid in quantity is somewhat expensive, it will generally be best to buy from dealers and test for purity. When small quantites are needed, either in gas or liquid form, a cylindrical leaden vessel with lid may be employed, of sufficient size tosupport on a tall leaden tripod the platinum crucible or dish, which is to contain the water to absorb the gas, when liquid acid is wanted, or to contain in fine powder the mineral to be decomposed by the acid gas.

On the bottom of the leaden vessel a mixture of two parts of powdered kryolite, with five parts of concentrated pure sulphuric acid, is spread; the tripod is placed in position, and on it the platinum vessel; the lid is loosely laid on, and gentle heat is employed to evolve the gas from the mixture. When fluorspar has to be used instead of kryolite, the first portion of the gas must be suffered to escape before the platinum vessel is put on the tripod, so as to get rid of the silicium tetrafluoride liable to form from silicates, which often occur in commercial fluorspar. Great care should be taken to avoid inhaling the gas or to prevent the liquid from coming in contact with the skin

HYDROFLUOSILICIC ACID, H_2SiF_6.

USED to separate barium from strontium, and occasionally to detect potassium. Also in micro-petrographic work.

TESTS. It must give no precipitate with strontium sulphate solution. It must leave no crystalline residue on evaporation.

PREPARATION. Into a flask of half a litre capacity there is introduced a mixture of twenty-five grammes each of fine quartz sand and powdered pure fluor spar or kryolite, with 125 Cc. of pure concentrated sulphuric acid. The flask is closed by a cork, through which a wide glass tube passes, bent twice at right angles, whose free end dips into a beaker containing half a litre of pure water. When the flask is gently heated, silicon tetrafluoride gas is evolved, which in contact with the water is at once decomposed according to the following equation:

$$3SiF_4+3H_2O = 2H_2SiF_6+H_2SiO_3.$$

The gelatinous silica thus formed surrounds each gas bubble as it enters the water, and necessitates continual stirring to prevent the formation of channels through which the gas can escape undecomposed, or the clogging of the delivery tube. It is best to either enlarge the end of the delivery tube by attaching thereto a small funnel tube, or else to pour some mercury into the beaker, just sufficient to let the end of the delivery tube reach under its surface. When gas is no longer evolved, the gelatinous mixture of silica and hydrofluosilic acid is separated by filtration, first through a clean linen strainer, then through filter paper, and the acid is preserved in small glass stoppered vials in a cool place. As the glass flask is corroded, so as to be unfit for subsequent use, it is best to make a full supply of acid at once.

HYDROSULPHURIC ACID, H_2S.

Hydrogen Sulphide or Sulphuretted Hgdrogen.

USED as a general reagent to separate metals into groups, and to identify some by the characteristic color of their sulphides.

It is either used by passing the gas directly into the metallie solutions, or by adding to them a saturated solution of H_2S in pure water.

TESTS. Water saturated with pure H_2S leaves no residue on evaporation, does not form a precipitate on addition of ammonia, gives a copious precipitate of sulphur on addition of ferric chloride, and must have the strong characteristic odor of the gas in full strength.

To insure purity, it is best to use in its preparation only pure ingredients, and to pass the gas through a suitable wash bottle to deposit impurities mechanically carried over from the apparatus.

PREPARATION. Ferrous sulphide is treated in a suitable apparatus with pure dilute sulphuric or hydrochloric acid.

To obtain good ferrous sulphide, put cuttings of clean sheet iron or nails into a hessian crucible, heat to a full white heat, then add pure sulphur in small lumps until the mass is fused, and pour into a suitable clean mould.

Many varieties of apparatus have been devised for making sulphuretted hydrogen. A very simple one may be constructed by taking a stout wide mouth bottle, perforating its cork twice, passing through one of the perforations a funnel tube reaching nearly to the bottom, through the other a glass tube bent twice at right angles, whose short end just reaches through the cork, while the longer passes through the cork of a smaller wide mouth bottle, under the surface of the water with which it is about half filled; while another tube, also bent twice at right angles, rises from above the water to conduct the washed gas into the receiving vessel, which is nearly filled with pure, cold water. Into the larger bottle a sufficient quantity of ferrous sulphide, broken into small lumps, is placed and the dilute acid poured in through the funnel tube. All joints must be perfectly tight.

To ascertain whether the water is saturated with the gas, close the bottle and shake it well. If the water still absorbs a portion of the gas enclosed, a vacuum will result, indicated by an inward rush of air on reopening the bottle. Before sealing the small bottles, in which the solution is to be preserved, displace the air above the liquid with hydrogen sulphide.

IODIC ACID HIO_3, and IODINE PENTOXIDE I_2O_5.

USES. Iodic acid is used in analysis of alkaloids (e. g. to distinguish morphine from codeine). It is sometime kept as anhydride, iodine pentoxide, I_2O_5, and dissolved when needed, or else it is made for immediate use by mixing potassium iodate with sulphuric acid.

TESTS. The anhydride, I_2O_5, is a white crystalline powder, which at 300° C. is decomposed into iodine and oxygen, leaving no residue. It is easily soluble in water, forming iodic acid. Its solution must not color starch solution.

PREPARATION. Dissolve iodine in very concentrated nitric acid. Evaporate to dryness, so as to volatilize any surplus, of either acid or iodine, not exceeding a temperature of 200° C. Dissolve the yellow residue in water. Evaporate again to dryness, and then keep

the residue at 200° C. until the color has become white. The pentoxide thus formed is dissolved in ten parts of distilled water, as it is needed.

META-DIAMIDO-BENZOIC ACID, $H\,C_7\,H_7\,N_2\,O_2 + H_2\,O$.

USES. With nitrous acid it is colored intensely yellow, and forms, when dissolved in sulphuric acid, a most delicate reagent for traces of nitrites. (*Griess.*)

TESTS. The long needle-shaped crystals are sold of sufficient purity.

PREPARATION. As the solution decomposes by long standing, only enough may be prepared for present use by dissolving one part in about 100 parts of very dilute sulphuric acid.

META-TUNGSTIC ACID, $H_2\,W_4\,O_{13} + 8\,H_2\,O$.

Meta-Wolframic Acid.

USES. *Scheibler* recommended the use of the free acid and of the sodium salt, as well as the *phospho-wolframic acid* (see under phosphoric acid) for analysis of alkaloids, some of which it precipitates, but offers no advantage over other reagents. It is sold of sufficient purity by dealers.

MOLYBDIC ACID, $H_2\,Mo\,O_4$.

AND DERIVATIVES.

Molybdic acid and its sodium and ammonium salts are now supplied in commerce perfectly pure, and at such rates that their preparation and purification from the crude mineral is not advantageous.

a. SODIUM PHOSPHOMOLYBDATE, $Na_3\,PO_4\;10\,Mo\,O_4$ (also 11 and 12 $Mo\,O_4$) in nitric acid solution.

De Vry's or Sonnenschein's Reagent.

USES. Produces in solutions of ammonium salts and alkaloids yellow precipitates.

PREPARATION. Dissolve 1.5 grammes sodium molybdate and 0.36 grammes sodium phosphate in 14 Cc. boiling water, then add nitric acid, of spec. gr. 1.42, sufficient for 16 Cc. Preserve in closely stopped vials, to prevent contact with ammoniacal vapor.

b. SULPHO-MOLYBDIC ACID, OR MOLYBDENYL SULPHATE, $Mo\,O_2\,SO_4$.

Froehde's Reagent.

USES. Produces characteristic colors with morphine, codeine, narcotine, etc.

PREPARATION. Immediately before using dissolve in 1 Cc. conc. pure sulphuric acid about 5 milligr. of molybdic acid or 5.5 mgr. of sodium molybdate.

c. AMMONIUM MOLYBDATE solution in nitric acid $(NH_4)_2$ Mo O_4.

USED for precipitation of phosphoric acid.

PREPARATION. Dissolve one gramme finely powdered ammonium molybdate in 6.7 Cc. of hot water (if the salt has lost ammonia by long keeping, a little ammonia water must be added), and pour this solution into 6.7 Cc. of pure nitric acid of spec. gr. 1.2 (made by mixing 3.3 Cc. of pure nitric acid of spec. gr. 1.42 with 3.4 Cc. of distilled water). It does not answer so well to pour the acid into the aqueous solution. Preserve in the dark.

For washing precipitates, one volume of this solution is diluted with three vol. of pure water.

NOTE. In most cases it is not advantageous to prepare this salt on a small scale from the ore. Where, however, either molybdenite, Mo S_2, or molybdenum ochre, Mo O_3, or lead molybdate, Pb Mo O_4, can be obtained cheaply, the pure acid or the ammonium salt may be prepared as follows:

Lead molybdate is finely powdered, and then digested for some days with very dilute hydrochloric acid to remove carbonates accompanying it. The powder is separated and boiled with concentrated hydrochloric acid. After cooling, the solution of molybdic acid is decanted from the lead chloride, a small amount of sulphuric acid is added to precipitate most of the remaining lead, the liquid is filtered through asbestos, and, after addition of some nitric acid, is evaporated to dryness. The product is impure molybdic acid, and it must be purified in the same manner as the native impure acid occurring as molybdenum ochre. The finely powdered substance is digested at a temperature of about 20° to 25° C. with ammonia water, being frequently stirred. When the acid has been dissolved, a small amount of ammonium sulphide is added to precipitate lead, etc. It is then filtered, concentrated by evaporation, and set aside to crystallize. The crystals are purified by recrystallization. When molybdenite (molybdenum glance) is used, it is finely powdered, mixed with pure sand and roasted in a muffle, scorifier or platinum dish. To oxidize fully, the mixture must be frequently stirred, so as to expose it freely to access of air while heated to a red heat. Sulphur is volatilized as SO_2, while molybdic acid is formed, which, when finished, will appear lemon yellow while hot, but white when cooled. It is treated for purification like the impure acid obtained from other ores.

NITRIC ACID, HNO_3.

USED as a solvent of silver, mercury and other metals, as an oxidizer of ferrous and other salts, and to detect bile colors, uric acid, brucine and other alkaloids by characteristic color reactions.

TESTS. It should be colorless, leave no residue on evaporation, give, when diluted, no precipitate with silver nitrate (abs. of chlorine), nor with barium nitrate (absence of sulphate).

After neutralization it must not give a precipitate with hydrogen sulphide or ammonium sulphide (abs. of metals).

It must show absence of arsenic by Fleitmann's test, i. e., on adding potassium hydrate in considerable excess of neutralization and boiling the mixture with pure zinc or aluminium, the gas evolved must not blacken paper moistened with silver nitrate solution.

After dilution it must not color starch solution blue or chloroform violet, even after adding a little hydrogen sulphide or sulphurous acid (abs. of iodides and iodates).

PREPARATION. To commercial nitric acid a solution of silver nitrate is added as long as a precipitate falls, and then in slight excess. The clear liquid is decanted from the precipitate and carefully distilled, leaving a small residue in the retort. Pure nitric acid of the U. S. P. strength, spec. gr. 1.42, is needed for bile tests. For most other purposes, mix equal volumes of the strong acid and distilled water, or obtain pure acid of spec. grav. 1.2. The strong acid is easily decomposed by light, and then contains nitrogen tetroxide and lower oxides, and becomes yellow.

Red Fuming Nitric Acid is a concentrated nitric acid charged with nitrogen tetroxide, and may be prepared by placing a mixture of 100 grammes of potassium nitrate (absolutely free from chloride) and 1.5 grammes starch into a tubulated retort of 1 litre capacity, connecting with a suitable refrigerator, and adding a mixture of fifty grammes each of pure concentrated sulphuric acid and pure fuming sulphuric acid. The distillate may be received separately, or, if not needed of such concentration, into a receiver containing 100 Cc. of pure concentrated nitric acid. At first the heat evolved by the mixture is sufficient, afterwards a gentle heat may be applied to finish the distillation.

A much simpler mode will furnish an acid of less purity, but useful for some purposes. Nitrogen dioxide is evolved from a flask containing copper chips and nitric acid, the gas is passed first into a washbottle filled partly with nitric acid, so as to convert it into tetroxide, and from thence into the receiver. In this strong nitric acid is contained, which is gradually saturated with the gas.

Sometimes pure sulphuric acid is thus saturated with *nitrogen tetroxide* and used in the analysis of iodides.

Concentrated red fuming nitric acid is used to oxidize sulphur into sulphuric acid and sulphides into sulphates, also to liberate iodine from iodides.

Normal Nitric Acid is occasionally used for alkalimetric determination of the hydrates and carbonates of alkaline earths. It is prepared by diluting a stronger acid with pure water until it corresponds in strength with a normal alkali solution. It contains 62.91 grammes of HNO_3 in one litre.

NITRO-HYDROCHLORIC ACID.

Nitro-Muriatic Acid or Aqua Regia.

USED as a solvent of gold, platinum, etc., to decompose mercuric and other sulphides, and as a source of chlorine.

PREPARED by mixing one volume of nitric acid of spec. grav. 1.42 with 3.3 vol. hydrochloric acid of spec. grav. 1.16.

Nitroxyl chloride, NO_2Cl, nitrosyl chloride, NOCl, and free chlorine are formed:

$$2\,HNO_3 + 4\,HCl = NO_2Cl + NOCl + Cl_2 + 3\,H_2O.$$

The mixture must be kept cool. After effervescence has ceased the acid is preserved in a cool place, in small vials, not entirely filled.

OSMIC ACID ANHYDRIDE, OsO_4.

Osmium Tetroxide; Perosmic Acid.

USES. It liberates iodine from iodides. A 1% solution is used in microscopical work to stain nerve fibres black, and thus differen tiate them from surrounding tissues.

The commercial article is of sufficient purity. It is very poisonous, and should be handled with extreme caution.

OXALIC ACID, $H_2C_2O_4 + 2H_2O$.

USES. In qualitative analysis the free acid is but rarely employed for precipitation of calcium salts, etc.; for microchemical work solutions of various strengths are in use. A *normal volumetric* solution is used in alkalimetry, and a deci-normal one as a companion to deci-normal solution of potassium permanganate.

TESTS. Oxalic acid forms colorless, transparent, clinorhombic prisms, soluble in 14 parts of water at 15°C. On exposure to dry, warm air it loses water of crystallization and forms a white powder. On being heated on platinum foil, it should completely volatilize without emitting odor of burnt sugar, or leaving any residue. It should not blacken by heating with concentrated sulphuric acid. A cold, saturated solution in water should not become turbid by mixing with an equal volume of cold alcohol.

PREPARATION. To obtain pure oxalic acid from the crude commercial article, 1 part of crude acid is dissolved in 10 parts of distilled water at 15°C. This leaves a considerable quantity undissolved, among which are most of the impurities. The saturated solution is filtered off, concentrated to three-fourths of its volume and set aside to crystallize. The alkaline oxalates yet present crystallize with this first portion. The motherlye, which now contains only pure oxalic acid, is carefully decanted, concentrated and left to crystallize, being occasionally stirred to prevent the formation of large crystals which might enclose moisture. The crystals are now drained on a funnel, and lastly dried on blotting paper. Thus purified, the acid contains two molecules of water, which it retains unchanged so long as it is kept in close bottles at ordinary temperatures, so that its composition may be strictly relied upon for quantitative work.

Normal Solution of Oxalic Acid

is obtained by dissolving 62.86 grammes (63) of carefully selected crystals of $H_2C_2O_4 + 2H_2O$ in distilled water, so as to make 1 litre. Control by testing with normal alkali solution. Deci-normal solution is made by appropriate dilution.

PERCHLORIC ACID, $HClO_4 + 2H_2O$.

USES. From solutions of potassium salts it precipitates potassium perchlorate, 1 part of which at 15°C. is soluble in 70 parts of water, insoluble in alcohol. The crystals are rhombic and are of importance in microscopic determination of potassium. It is also a special reagent (*Fraude's*) for aspidospermine, which it colors intensely red, while strychnine is colored a reddish yellow and brucine a dark brownish yellow; other alkaloids give no reaction.

TESTS. Pure, anhydrous perchloric acid is a colorless liquid, fuming in air, spec. grav. 1,782, very corrosive. It cannot be preserved in this state many days, as it decomposes, becomes colored and spontaneously explodes. When united with 2 molecules of water the acid may be safely preserved, and forms a syrupy liquid, boiling at 203°C. The somewhat more dilute article furnished by dealers in chemicals is of sufficient purity.

PREPARATION. Pure potassium chlorate is carefully heated to about 400°C., when after fusing to a thin liquid it loses a portion of its oxygen and becomes thick. It is now removed from the fire, the KCl extracted by cold water, and then recrystallized from a saturated boiling solution, when $KClO_4$ deposits first in small rhombic crystals. These are dried and 1 part mixed with 4 parts of conc. sulphuric acid and distilled. The distillate is purified by redistillation at 110°C., and 5 parts of it are diluted with 2 parts of distilled water.

PHOSPHORIC ACID AND DERIVATIVES.

a. ORTHO-PHOSPHORIC ACID, H_3PO_4.

Tribasic Phosphoric Acid.

USED occasionally to set free volatile acids from their salts (as acetic acid from calcium acetate) so as to separate them by distillation without admixture with another volatile acid; also in testing for alkaloids it colors aconitine and digitalin violet; also to prepare compound phosphoric acids (phospho-molybdic, phospho-wolframic, etc.) The anhydride, P_2O_5, is used for dehydration. For most purposes the U. S. P. solution, containing 50 per cent of H_3PO_4, of sp. gr. 1.347, may be used.

TESTS. The absence of arsenic must be proven in similar manner as in hydrochloric or nitric acid, potassium permanganate solution having first been added drop by drop until no longer decolorized, so as to oxidize any phosphorous acid present. Silver nitrate should produce no precipitate in phosphoric acid diluted with 5 parts of water. A brown or black precipitate would indicate phosphorous acid; a white, hydrochloric.

Indigo solution must not lose its color by heating with diluted phosphoric acid, nor should a cooled mixture of solution of ferrous sulphate with concentrated sulphuric acid show a dark color at the zone of contact when phosphoric acid is carefully poured upon it (absence of nitric acid).

Hydrogen sulphide must produce no precipitate in diluted phosphoric acid saturated with the gas, even after standing for ten or twelve hours. Neither albumen nor barium chloride should produce a precipitate (absence of sulphuric and of metaphosphoric acids).

b. METAPHOSPHORIC ACID, HPO_3.

USES. To detect albumen, with which it forms a white precipitate. For use in urine analysis, a solution of 1 part of glacial phosphoric acid in 10 parts of water and 1 part of acetic acid is recommended. In blow-pipe work the free acid is now rarely used, the sodium salt obtained from microcosmic salt being preferred.

The commercial glacial phosphoric acid is sufficiently pure for these purposes.

c. PHOSPHO-ANTIMONIC ACID.

Schulze's Reagent.

USED but rarely as a general precipitant of alkaloids, being less delicate than sodium phospho-molybdate (see molybdic acid, etc.),

except with atropine. Brucine is precipitated with rosered color, dissolved by heating; other alkaloids and ammonia white; caffeine is not precipitated.

PREPARED by adding 1 Cc. antimonic pentachloride (obtained by heating pure powdered antimony in a rapid current of chlorine gas) to a mixture of 1 Cc. pure, 50 per cent phosphoric acid with 2 Cc. of water; or 1 Cc. antimonic chloride with 3 Cc. of a saturated solution of sodium phosphate, and decanting from any precipitate which may have formed after standing.

d. PHOSPHO-TUNGSTIC OR PHOSPHO-WOLFRAMIC ACID.

Scheibler's Reagent.

USED, like the preceding, for precipitation of alkaloids, but does not offer any advantages over phospho-molybdic acid or sodium meta-wolframate (meta-tungstate).

PREPARED by dissolving 1 gramme sodium tungstate, $Na_{10}W_{12}O_{41} + 28H_2O$, in 10 Cc. water, and adding 1 Cc. pure phosphoric acid of U. S. P. strength.

PICRIC ACID, $C_6H_2(NO_2)_3OH$.

Carbazotic Acid, or Tri-Nitro-Phenol.

USED in detection of albumen, glucose and alkaloids.

The commercial article is sufficiently pure when in distinct crystals.

PREPARATION. As picric acid is liable to explode when suddenly heated it should be prepared with great caution. Nine parts of crystallized phenol are dissolved in 10 parts concentrated sulphuric acid, so as to form phenol sulphonic acid. To this there are gradually added 45 parts of nitric acid of specific gravity 1.42, previously diluted with 20 parts of water. At the end of the reaction the mixture is carefully neutralized with potassium carbonate. The potassium picrate (requiring 340 parts of water for solution of 1 part) precipitates. The precipitate is separated and purified by recrystallization from boiling water. At last, dilute sulphuric acid is added, so as to liberate the picric acid; the crystals are separated, washed with a little water and recrystallized for purification, if necessary.

For use, 1 centigramme is dissolved in 10 Cc. hot distilled water, and, if necessary, filtered after cooling.

PYROGALLIC ACID, $C_6H_3(OH)_3$.

Pyrogallol.

USED in alkaline solution to absorb oxygen; with sulphuric acid to detect minimal quantities of nitric and nitrous acid, e. g., in

drinking water. Also to detect glycerin by boiling the liquid with a few crystals of pyrogallic acid and some sulphuric acid, then diluting and adding stannic chloride, when the presence of glycerin is indicated by a reddish violet color (*Reichl*).

The white crystals of the commercial article are sufficiently pure.

ROSOLIC ACID, $C_{20}H_{16}O_3$, and AURIN or PARAROSOLIC ACID, $C_{19}H_{14}O_3$,

as well as the *yellow corallin*, which contains them, are used as indicators in alkalimetry, especially for free ammonia. It also suits well for all mineral acids and oxalic, but not so well for other organic acids. 1 gramme is dissolved in 100 Cc. very dilute alcohol. The solution turns violet-red with alkalies, yellow with acids.

SALICYLIC ACID, $H\,C_7H_5O_3$.

This acid is rarely used as a reagent. Flueckiger proposes it to detect oil of peppermint, which, with the fused acid, is colored bluish-green. If alcohol be added the solution becomes dichroic, blue with transmitted, red with reflected light. The commercial article is sufficiently pure for this purpose.

SILICIC ACID, H_2SiO_3.

USES. Silicic acid, as well as silicon dioxide, SiO_2, is occasionally used as a flux in blowpipe work. The precipitate obtained in making hydro-fluo-silicic acid, when sufficiently washed and dried, consists of pure acid.

SILICO-TUNGSTIC ACID, $H_8W_{12}SiO_{42} + 29\,H_2O$.

Godeffroy's Reagent.

USED as a very delicate reagent for the precipitation of alkaloids from dilute solutions.

PREPARATION. Boil 60 parts of crystals of commercial sodium tungstate, $Na_{10}W_{12}O_{41} + 28\,H_2O$, with 1 part of freshly precipitated silicic acid, for about an hour, with 200 parts of water. Filter; heat the filtrate again to boiling, and add a slight excess of freshly prepared mercurous nitrate solution. Mercurous silico-tungstate precipitates, which is washed on a filter, and then decomposed with a sufficient amount of hydrochloric acid to decompose the salt. Mercurous chloride remains as a residue, and the filtrate on evaporation forms transparent, yellowish, quadratic, octohedral crystals, of the composition $H_8W_{12}SiO_{42} + 29\,H_2O$. One part of these is dissolved for use in 10 parts of distilled water.

A less pure acid may be obtained more readily by omitting the precipitation by mercurous nitrate and decomposing the solution of sodium silico-tungstate directly with hydrochloric acid.

SULPHANILIC ACID, $NH_2C_6H_4SO_3H + 2H_2O$.

Aniline-Para-Sulphonic Acid.

USED in conjunction with naphthylamine sulphate to detect small amounts of nitrites by the production of an intense red color (*Griess*). It is converted by addition of nitrous acid into

Di-azo-benzol-sulphonic acid, or Benzol-sulphon-diazide,

which is employed to produce *Ehrlich's Diazo-reaction* in urine. Also as a delicate test for bilirubin, and, in connection with sodium amalgam, to detect aldehydes. The test solution for urine and bilirubin is made as follows: 12 to 15 Cc. of nitric or hydrochloric acid are diluted to 350 Cc. with pure water, and then saturated with sulphanilic acid. Just before using, 5 Cc. of a solution of 1 part of sodium nitrite in 200 parts of water are added. Equal parts of this mixture and the urine are then mixed with a few drops of ammonia water. After standing for some hours, normal urine shows a deeper yellow or orange color, which, however, is not intense enough to stain the foam. The deposited earthy salts are not colored. In the urine of typhoid fever, measles and phthisis, a characteristic red color is developed, plainly visible in the foam, while the deposit of earthy salts assumes a green to violet color.

To detect bilirubin, urine is mixed with equal volumes of dilute acetic acid (6 per cent) and the reagent. If turbidity renders it necessary, strong acetic acid may be used in addition. A violet-red color shows the presence of bilirubin. Or the urine is shaken with chloroform, which dissolves the bilirubin. The chloroform solution is removed and mixed with about double its volume of the reagent, and enough alcohol added to make a clear solution. At first a yellow color appears, quickly changing to red. If now strong hydrochloric acid is added, the color changes through violet and purple tints to a pure blue, which remains for some time. Addition of sodium hydrate changes the blue to a greenish and red color.

It is also used in connection with sodium amalgam to detect aldehydes. With these a red color is produced, changing to violet (*Fischer and Penzold*). It is prepared by dissolving 2 parts of sulphanilic acid in about 15 parts of normal sodium hydrate, adding 1 part of sodium nitrite and pouring the solution into 20 parts of cold normal sulphuric acid. Small needle-shaped crystals precipitate, which must be dried on filter paper and preserved in a cool place, as a temperature of 60° C. causes them to decompose. When mixed with ammonia, they violently explode.

TESTS. The acid forms colorless, rhombic prisms, which easily lose water of crystallization; it is soluble in 182 parts of cold water.

It is obtained of sufficient purity from dealers or by preparing it according to the following directions:

PREPARATION. On the small scale, sulphanilic acid may be prepared by heating 1 part of pure aniline oil with 2 parts of fuming sulphuric acid, and purifying the product by repeated recrystallization.

Also by decomposing commercial Helianthin, called also Orange III, and consisting of sulpho-dimethyl-amido-azo-benzol, $(CH_3)_2N.C_6H_4.N:N.C_6H_4.SO_3H$, by a reducing agent into sulphanilic acid and para-amido-dimethyl-aniline. As the latter is used as a most delicate reagent for hydrogen sulphide, a process for the preparation of both is here given.

One part of helianthin is triturated with five parts of water and 2 parts of freshly prepared ammonium sulphide, and heated on a water bath. Sulphanilic acid and para-amido-di-methyl-aniline are formed, the first of which is insoluble in ether, the latter soluble. The solution is therefore shaken with ether, left to stand a little while, and the ethereal layer separated; the operation being several times repeated, so as to use an amount of ether about equal in bulk to the solution. The united ethereal layers are digested with white lead to remove ammonium sulphide, filtered and mixed with concentrated sulphuric acid, previously dissolved in an equal bulk of ether. The mixture is set aside to form crystals of *sulphate of para-amido-dimethyl-aniline*, which is preserved as a reagent for H_2S. After removal of the ethereal solutions, the residue containing the sulphanilic acid is heated to boiling to remove ammonium sulphide and set aside to deposit the acid, which may be purified by recrystallization.

SULPHURIC ACID, H_2SO_4.

USES. Sulphuric acid is used in a variety of chemical operations. For some, the crude oil of vitriol of commerce suffices, as for drying, etc.; for others, the pure acid, either in concentrated or dilute state, is employed. Among its applications are: neutralizing alkalies; liberating nitric, hydrochloric, boric, phosphoric and other acids from their salts; recognition of oxalic and other organic acids by their decomposition products; evolution of hydrogen, hydrogen sulphide, arsenetted hydrogen and other gases; detection of lead, barium and strontium, etc.

A small amount of nitric acid in concentrated sulphuric acid is used as *Erdmann's Reagent* in the analysis of alkaloids, and is prepared as follows: 1 drop of nitric acid of spec. grav. 1.25 is dissolved in 16 Cc. water. Of this solution 10 drops are added to 20 grammes pure concentrated sulphuric acid.

The concentrated commercial acid (*oil of vitriol*) is, on account of its manufacture from pyrites, so often contaminated with arsenic that for most purposes of analysis it is best to buy the pure acid, which is now made on the large scale, in platinum stills, so cheaply that it is not profitable to incur the trouble and risk of preparing it by redistilling the crude acid from glass on a small scale.

TESTS. Pure concentrated sulphuric acid should contain at least 96 per cent of H_2SO_4 and have sp. gr. 1.840. It should be colorless, and must be protected from dust and moisture in well closed, glass-stoppered bottles.

It must show absence of the nitrogen acids by leaving colorless at the zone of contact with the conc. sulphuric acid dilute solutions of ferrous sulphate, brucine, di-phenyl-amine, meta-phenylen-diamine, para-toluidine or pyrogallic acid. It must, after dilution with much water, not color blue a dilute solution of potassium iodide and starch (nitrous acid).

To show absence of arsenic and of sulphurous acid place 5 Cc. of diluted acid into a test tube, add a few granules of pure zinc, and cover the test tube with a cap of filtering paper, moistened with a drop of silver nitrate. Blackening of the silver indicates arsenic or sulphurous acid. If lead acetate be used instead of silver nitrate to moisten the paper, blackening occurs only if sulphurous acid is present, which is reduced to hydrogen sulphide by the nascent hydrogen.

Absence of lead is shown by carefully pouring upon a few Cc. of sulphuric acid in a test tube some hydrochloric acid. A white turpidity at the zone of contact shows the presence of lead, while pure acid remains clear. The sulphuric acid remaining clear when mixed with about 4 volumes of pure alcohol indicates the absence of lead, lime and iron.

Selenous acid is shown by a red precipitate of selenium, when sulphurous and hydrochloric acids are added in small quantity.

On saturation with ammonia and ignition on platinum foil no residue should remain.

PREPARATION. When it becomes necessary to purify commercial acid in the laboratory, the nitrogen compounds are first removed by mixing in a large porcelain dish 1 litre of the acid with about 6 grammes of ammonium sulphate and heating the mixture until copious white vapors of acid arise.

To remove arsenic it is necessary to convert its trioxide, which easily volatilizes at the boiling point of the acid, into pentoxide, which does not pass over with the sulphuric acid during distillation. Hence, before the acid has fully cooled, 10 grammes of manganese dioxide are added, and the mixture heated to the boiling point.

After cooling. the clear liquid is separated and introduced into a glass retort of from 2 to 3 litres capacity, whose outside had been previously coated with clay, and carefully distilled. After rejecting the first few Cc. of distillate, the distillation is continued until 750 Cc. have passed over.

Dilute sulphuric acid may be prepared by carefully adding 10 Cc. concentr. sulphuric acid of spec. gr. 1.840 to 174 Cc. of pure water.

For volumetric purposes, *normal sulphuric acid*, containing 48.915 grammes $H_2 S O_4$ in 1 litre, is prepared by carefully diluting the stronger acid so as to accurately saturate an equal volume of normal alkali solution. It may be controlled by precipitating with barium chloride, and weighing the precipitated barium sulphate. 100 Cc. normal sulphuric acid correspond to 11.63 grammes barium sulphate.

Mol. weight of $H_2 S O_4$—97.824.

SULPHUROUS ACID, $H_2 S O_3$.

USED to reduce gold, silver and mercury from their salts; to convert cupric into cuprous salts, chromic acid into chromic oxide, etc.

PREPARED by saturating pure water with pure sulphur dioxide gas, of which about 9.5 per cent will dissolve at ordinary temperature, producing a solution of sp. gr. 1.023.

Pure sulphur dioxide is best obtained by heating pure sulphur or copper with pure sulphuric acid. The solution must be carefully protected from light and air; if preserved too long, sulphuric and pentathionic acids are liable to form. When made by boiling charcoal with sulphuric acid it will contain carbonic acid.

TESTS. It must be perfectly clear and colorless, and strongly saturated with $S O_2$. It should not precipitate barium chloride previously acidulated with hydrochloric acid.

On evaporation on platinum foil it must leave no residue. If not known to be made from pure materials, it must be tested for arsenic by the methods already described.

TANNIC ACID, $H C_{14} H_9 O_9$.

Digallic Acid or Tannin.

USED to precipitate alkaloids, gelatin, albumin, starch; also ferric and vanadic salts (blue-black). One drop of its 10% solution added to 1 Cc. of centinormal iodine solution forms *Griessmayer's test* for alkaline hydrates, with which it produces a red color.

TESTS. Pure tannic acid burns completely, leaving no residue. With water it must yield a clear, colorless solution, not precipitable by alcohol. A solution of 1 part in 5 parts of boiling water must

remain clear on addition of a double volume of strong alcohol (absence of gum, dextrine, etc.), also on addition of a double volume of cold water (abs. of resins).

PREPARATION. Select a pale yellow, light article of commercial tannin, with but little odor, tested for purity as above, dissolve 1 part in 5 parts of cold water, filter and fill up to 10 parts with 10% alcohol. If preserved in solution too long it will decompose, forming gallic acid.

TARTARIC ACID, $H_2C_4H_4O_6$.

USED occasionally to prevent the precipitation of ferric oxide and alumina by caustic alkalies, while other members of the third and fourth group are precipitated. Also for acidulation of organic mixtures in toxicological examinations and to precipitate potassium as acid tartrate, for which purpose, however, sodium acid tartrate is preferable. To detect iodates in presence of iodides by the yellow color surrounding the crystal.

On account of rapid deterioration of the solution by mould, it is kept in a dry state until required, when 1 part is dissolved in 2 parts of pure water (or in 5 parts according to U. S. P.)

TESTS. The crystallized acid of commerce is generally found sufficiently pure.

It should leave no residue on ignition.

It should yield no precipitate with calcium sulphate (absence of oxalic acid); nor with silver nitrate (abs. of chlorides); nor with barium chloride acidulated with hydrochloric acid (abs. of sulphates). Mol. W.=149.656.

TITANIC ACID, H_4TiO_4.

USES. Dissolved in concentrated sulphuric acid it gives a red brown color to morphine, being a most delicate reagent for it (Flueckiger). It also gives with hydrogen dioxide and with barium dioxide a very characteristic yellow color, not communicable to ether. For this reaction a solution in concentrated sulphuric or hydrochloric acid is made, containing 1.5 milligr. titanic acid in 1 Cc.

PREPARATION. The minerals rutile, brookite and anatase consist of more or less pure titanic acid. They are finely powdered, mixed with 10 parts of potassium di-sulphate, and heated in a platinum crucible until a clear, glassy mass results. This is powdered and extracted with cold water. A drop of sulphuric acid is added to the filtered solution, and then hydrogen sulphide passed through for some time. The solution is again filtered, and then heated to boiling for about an hour, while a current of carbonic acid gas is passed

through it, the water lost by evaporation being occasionally replaced. This precipitates the titanic acid, which is collected on a filter and is sufficiently pure for use.

TRICHLORACETIC ACID, $HC_2Cl_3O_2$.

USED to detect albumen in urine. A crystal thrown into urine containing albumen surrounds itself with a white coagulum (*Raabe*).

TESTS. The acid forms transparent rhombohedric crystals, which easily deliquesce, melt at 52.3° C., boil at 195° C. When heated with potassium hydrate solution, chloroform and carbonic acid gas are formed.

PREPARATION. Mix thoroughly a solution of 15 parts of chloral hydrate in 15 parts of water, with a solution of 8 parts of potassium permanganate in 32 parts of boiling water. The result is the oxidation of the trichloractic aldehyd (chloral) into the corresponding acid, which unites with the potassium, while manganese dioxide precipitates. The mixture is filtered, then supersaturated with strong (glacial) phosphoric acid and distilled. From the distillate the crystals are separated, and, if necessary, purified by redistillation.

Chloral hydrate may also be converted into trichloracetic acid by oxidation with red fuming nitric acid in direct sunlight. 1 part of chloral hydrate is added to 4 parts red fuming nitric acid, exposed to direct sunlight for several days, until no more red fumes are given off. The mixture is distilled and the crystals separated as before. They are somewhat more difficult to purify from accompanying nitric acid.

NOTE. Other acids, but rarely employed, or made extemporaneously by adding sulphuric acid to their salts, are

Formic Acid, $H.CHO_2$.

Used in *Hampe's* process for separating zinc from other metals. It is made by distilling at 100° C. a mixture of equal weights of crystallized oxalic acid and glycerin. The commercial article is sufficiently pure if entirely volatile.

Selenic acid, see *Sodium selenate.*

Selenous acid, see *Ammonium selenite.*

Vanadic acid, see *Ammonium metavanadate.*

ALBUMIN.

USES. To distinguish meta-phosphoric acid, which forms a precipitate with albumin, from ortho- and pyro-phosphoric acids. Also to remove tannin from mixtures, etc.

PREPARATION. The white of a hen's egg carefully separated from the yolk is shaken with about five volumes of pure water and filtered. Or the commercial dried albumin is dissolved in water.

ALCOHOLS.

AMYL ALCOHOL, $C_5H_{11}OH$.

Fusel Oil.

USES. Amylic alcohol is employed as a solvent of alkaloids, also to separate urobiline out of urine; also to separate lithium chloride from the chlorides of sodium and potassium.

TESTS. Even the purest article of commercial fusel oil contains several isomeric alcohols, difficult to separate. The greater part consists of iso-amylic alcohol $(CH_3)_2CH.CH_2.CH_2OH$, boiling, when pure, at 131,6° C., and of spec. grav. 0.811. It should be strictly neutral to moist test papers. On evaporation no residue must be left. Concentrated sulphuric acid should not give a brown color unless heat is applied; while cool, a variety of colors are produced, differing according to the proportions of acid and alcohol: 1 part of acid with 1 part alcohol, cherry red, passing into violet; with 5 to 6 parts of alcohol, blue; with 10 or more parts, greenish. Absence of pyridine and furfurol must be insured by rectification, as below described, as their presence would interfere with alkaloid reactions.

PREPARATION. For analytical purposes, amyl alcohol must be purified by shaking for some minutes 100 parts of the alcohol with 1 part of concentrated sulphuric acid, adding at once 10 parts of water; shaking again, and after a short period of rest draining off the amylic alcohol floating on the acid mixture. It is then digested over some calcium carbonate and hydrate, and then subjected to fractional distillation. All the portion coming over below 131° C. is rejected, and only the fraction boiling between 131° and 133° C. is preserved. By this cautious fractional distillation, alcohol free from pyridine and furfurol may be obtained, suitable for forensic analysis.

ETHYL ALCOHOL, C_2H_5OH.

Spirit of Wine.

USED as a general solvent of iodine, potassium or sodium hydrate, ammonia, ammonium sulphide, resins, organic acids, alkaloids and

various salts; also to separate substances soluble from those insoluble in it; to precipitate from aqueous solution calcium sulphate or malate, lead salts, etc.; to reduce oxides, to form with some acids, esters recognizable by characteristic odor, such as acetic, salicylic, etc.

It is employed either as *absolute* alcohol, of spec. gr. 0.7937, boiling at 78.4° C., or of U. S. P. strength, containing 91% by weight (94% by volume) of absolute alcohol, having spec. gr. 0.826 at 15.6° C.

For most analytical purposes the "*Cologne spirit*" of commerce is sufficiently pure.

TESTS. Pure alcohol must be miscible with water in all proportions without becoming turbid. It must be free from other alcohols (methylic, amylic, etc.), aldehyde and acids, hence, it must be entirely neutral to moist test papers; must not be colored on addition of potassium hydrate, conc. sulphuric acid, nor silver nitrate even after exposure to sunlight; no foreign odor must be perceivable on evaporation. It must show absence of furfurol by not assuming a red color, when 10 Cc. are mixed with 1 Cc. of colorless aniline oil and 0.5 Cc. hydrochloric acid (*Jorissen*).

PREPARATION. Redistil commercial alcohol, rejecting the first and last portions, then digest it for 24 hours with 1 gramme potassium permanganate for each litre and distil again.

The most concentrated alcohol obtainable by distillation alone has spec. grav. 0.825, and contains 89 per cent alcohol by weight. To remove the remaining 11 per cent of water, the alcohol may be digested with an excess of freshly calcined quicklime for several days, replacing the lime daily by a new supply, and finally distilling it carefully and slowly from a new portion of lime. The first four-fifths are quickly transferred to perfectly dry, glass-stoppered vials. If carelessly distilled the odor of lime will adhere to the alcohol, and moist test papers will show alkaline reaction.

Absolute alcohol must not change the white color of powdered anhydrous copper sulphate to blue. When shaken with a few milligrammes of anthraquinone and sodium amalgam the color must be green; a red color indicates the presence of water.

METHYL ALCOHOL, CH_3OH.

Wood Spirit.

USED occasionally instead of ethyl alcohol for solutions and separations, also for detecting salicylic acid by the characteristic odor of its methyl ester, and for separating boracic acid, which volatilizes completely by distillation with methyl alcohol.

PURIFICATION. Methyl alcohol is seldom found pure in commerce, being usually mixed with a large percentage of acetic acid, acetone, tar oils, etc. To free it from these it must first be distilled over an excess of quicklime. The distillate is mixed with powdered anhydrous calcium chloride, with which it forms crystals of $Ca\,Cl_2 + 2\,C\,H_4O$. These are separated from the liquid, dissolved in water and distilled, yielding an almost pure methyl alcohol, which is suitable for most purposes. To make it absolutely pure, methyl oxalate is prepared from it by distilling it with an equal weight of conc. sulphuric acid and twice its weight of potassium acid oxalate. Methyl oxalate, on cooling, forms colorless crystals, and these on redistilling with water yield pure methyl alcohol and oxalic acid.

TESTS. Absolute methyl alcohol boils at 65.5° C., and has specific grav. 0.798 at 20° C.

In 5 Cc methyl alcohol dissolve 0.1 gramme iodine and add solution of potassium hydrate till the brown color disappears. If acetone was present, a yellow precipitate of iodoform will fall.

The color of moistened test papers should not be changed.

GLYCERIN, $C_3H_5(OH)_3$.

Propenyl Alcohol.

USED as a solvent and to detect boracic acid by flame test, etc.

TESTS. Pure glycerin is a colorless, inodorous, thick liquid of sweet taste and neutral reaction, miscible with water in all proportions.

The best quality of the commercial article is sufficiently pure for use.

ALLOXANTIN, $C_8H_4N_4O_7 + 3\,H_2O$.

USES. To distinguish cotton from woolen fabrics. If a piece of mixed cloth is moistened with a solution of 1 part of alloxantin in 10 parts of warm water, dried, and then exposed to ammonia vapor, the woolen is colored crimson, the cotton remains white (*Overbeck*).

PREPARATION. One part of nitric acid, spec. gr. 1.42, is diluted with eight parts of water, heated to 60° C., and saturated with uric acid. It is then heated to boiling and a concentrated solution of stannous chloride, mixed with an equal volume of hydrochloric acid is added as long as a precipitate falls. An excess of stannous chloride is indicated by the production of a yellow color. The precipitate is collected on a filter, washed with very cold water, in which it does not readily dissolve, and then dried.

ALUMINIUM.

USES. The pure metal in the state of foil, ribbon or wire is used to generate pure hydrogen from a solution of potassium or sodium hydrate. Hence, it is employed in *Jatehouse's* modification of *Fleitmann's* test for arsenic. Also used to reduce nitric acid to ammonia.

TESTS. In a solution of potassium hydrate it must be soluble without residue. The gas evolved during the solution must not blacken paper moistened with silver nitrate or lead acetate solution.

ALUMINIUM SULPHATE, $Al_2(SO_4)_3 + 18 H_2O$.

USES. In microchemical detection of potassium salts, by forming with them alum crystals, recognized under the microscope by their octohedral form. Also to distinguish eosine from other dyes on textile fabrics. A hot solution of 1 part aluminium sulphate in 4 parts water removes the color of cochineal and other red lake dyes; coal-tar colors, such as corallin, fuchsin, saffranin, etc., are dissolved, while eosin remains unaffected (Dyer's Gazette). Also to precipitate albumen.

TESTS. The commercial salt, obtained by solution of clay or bauxite in sulphuric acid, or as a bye-product of the soda manufacture from kryolite is sufficiently pure, when free from iron.

PREPARATION. On the small scale it is obtained in precipating alum solution by ammonia, separating the aluminium hydrate by filtration, washing it thoroughly, and dissolving in pure sulphuric acid to neutralization.

NOTE. *Alum*, either the *potassium aluminium sulphate* or the corresponding ammonium salt, is sometimes, but rarely, used for similar purposes. The commercial salt, purified by repeated crystallization, or the U. S. P. salt may be used.

AMALGAMS.

These are alloys of various metals with mercury. The principal ones employed are *copper amalgam* for use with hydrobromic acid, to remove sulphur from sulphides, and *sodium amalgam* as a general reducent, by the introduction of nascent hydrogen, especially in organic compounds. They are described under the headings of the respective metals.

AMMONIA AND AMMONIUM COMPOUNDS.

AMMONIA, NH_3; AMMONIUM HYDRATE, NH_4OH.

Aqua Ammoniæ.

USES. The watery solution of ammoniacal gas, NH_3, usually called ammonium hydrate, is a reagent of great importance and general utility. It serves to neutralize acids, to precipitate the bases of many salts and to recognize some of them by characteristic colors; also to separate the insoluble hydrates of iron, aluminum, etc., from those of zinc, nickel, cobalt, copper, etc., which are soluble in ammonia; also to separate the soluble chloride, from the insoluble iodide of silver, etc., etc.; also as volumetric solution in acidimetry.

The U. S. P. prescribes two preparations of different strength: *Ammonia water* of spec. grav. 0.9593, containing 10% of gas in solution, and suitable for most purposes in analysis, and *stronger ammonia water* of spec. grav. 0.9026, containing 28% of gas in solution. Of the first 17 grammes saturate 100 Cc. normal acid solution, of the latter 6.07 grammes only are required. M. W.=17.021.

TESTS. The colorless solution must leave no residue on evaporation. It must be free from carbonate, hence, solution of calcium or of barium hydrate must not render it turbid. In ammonia supersaturated with nitric acid neither silver nitrate nor barium chloride must produce a precipitate (absence of chloride or sulphate). Hydrogen sulphide must produce neither coloration nor precipitate. Neither odor nor color must appear on neutralization with dilute sulphuric or hydrochloric acids, red color showing presence of pyrrol, brown of tar oils, etc.

PREPARATION. It will seldom be necessary to prepare ammonia on the small scale, as a very pure article is readily found in the market. When needed, 5 parts of freshly burnt lime are moistened sufficiently to slack and fall into powder. With this, 4 parts of granulated ammonium chloride are thoroughly mixed, and sufficient water added to form loose lumps. These are introduced into a flask, resting on a sand bath, and connected by glass-tubing without rubber joints, with one or, still better, two small wash bottles, and lastly, with a well-cooled receiver, containing ten parts of pure water. The wash bottles are partially filled with a small quantity of water, kept at a temperature of 90° to 98° C., so as to prevent the passage of pyrrol, aniline and similar volatile products into the receiver. The solution in the receiver is, at the close of the distillation, diluted to the required strength and kept in small vials, whose glass stoppers are coated with paraffin to prevent adhesion to neck.

Sometimes alcohol is saturated with the gas and used under the name of *Liquor Dzondii*. In connection with lead acetate, it serves to precipitate lactic acid. The U. S. P. *spiritus ammoniæ*, containing 10% of gas, is suitable for this purpose.

Volumetric Solutions of Ammonia.

The volatility of ammonia makes it difficult to preserve, for any length of time, a uniform amount of gas in concentrated solutions, and hence, though these are occasionally employed for special purposes, the half-normal solution is most frequently used on account of less liability to alter its titre, either from loss of gas or from absorption of CO_2 from the air.

Half-Normal Solution of Ammonia, containing 8.5 grammes NH_3 per litre. A stronger solution of ammonia is diluted until 100 Cc. accurately saturate 50 Cc. of Normal acid solution (either sulphuric, hydrochloric or oxalic), rosolic acid or cochineal solution being used as indicator.

Normal Solution, containing 17 gr. NH_3, and five-times normal, containing 85 gr. NH_3 in 1 litre, are occasionally used in water analysis, and prepared in same manner as the half-normal.

AMMONIUM BENZOATE, $NH_4C_7H_5O_2$.

USED in separating copper from cadmium; copper benzoate being soluble, cadmium insoluble in a 10 % solution of ammonium benzoate (*Gucci*).

TESTS. The U. S. P. salt is sufficiently pure. It forms colorless crystals, readily soluble in water and in alcohol. On heating they fuse, then give off vapors of benzoic acid and ammonia, and leave no residue. Its dilute solution should not, after acidulation with nitric acid, give a precipitate with barium chloride or silver nitrate.

PREPARATION. Dissolve 8.5 grammes of pure benzoic acid in sufficient ammonia water to neutralize accurately, and dilute with distilled water to 100 Cc., or make a 10% solution of the crystals.

AMMONIUM CARBONATE, $(NH_4)_2CO_3$.

USES. This reagent precipitates many metallic salts from their solutions as carbonates. It is especially employed in systematic analysis as the general precipitant of barium, strontium and calcium, which it serves to separate from magnesium and the alkalies. Also used to separate arsenic sulphide by solution from insoluble antimony sulphide, etc.

TESTS. After removing the outer crust of the commercial article (purified by resublimation), so as to reject the outer layer of ammonium dicarbonate and accidental impurities adhering to it, the crys-

talline mass must be completely volatilized by heat. It must be free from empyreumatic odor; after addition of a slight excess of nitric acid, neither hydrogen sulphide, barium chloride, nor silver nitrate, must produce a precipitate. A solution in water must not blacken ferric chloride.

PREPARATION. On the large scale, ammonium carbonate is made by subliming 1 part of crude ammonium chloride with two parts of chalk, or four parts of ammonium sulphate with four parts of chalk and one part of charcoal. This product must be resublimed, and, if not found in commerce of sufficient purity, must again be purified by careful resublimation. It consists principally of ammonium dicarbonate and ammonium carbamate: $NH_4HCO_3 + NH_4CO_2NH_2$. By solution in water, or in contact with moist air, the carbamate is converted into carbonate, and the dry commercial product, in undergoing this change, surrounds itself with a white pulverulent crust of dicarbonate. The inner crystalline part, shown to be free from chloride, sulphate, sulphide and hyposulphite, by the tests above described, is used for the solution by adding to 1 part of it a mixture of 1 part of 10% ammonia water with 4 parts of pure water. The solution contains neutral carbonate in about double normal strength (192 gr. in 1 litre).

A mixture of 391 Cc. of 10% ammonia water with 235 Cc. of this solution of carbonate is diluted with pure water to make 1 litre, and is much employed under the name of *Schaffgot's* solution in technical laboratories for the precipitation of magnesia in the analysis of alkalies.

AMMONIUM CHLORIDE, NH_4Cl.

Sal Ammoniac.

USES. The solution of ammonium chloride serves to retain in solution magnesium and manganous carbonates and hydrates, etc., while barium, strontium, calcium, aluminium, ferric salts, etc., are precipitated by ammonium carbonate and hydrate. From alkaline solutions it precipitates aluminium hydrate, etc.; from neutral and acid solutions, platinum and iridium as double chlorides. $NH_4Cl = 53.321$.

TESTS. Not a trace of residue must be left when ammonium chloride is heated on platinum foil. At ordinary temperatures it must form a perfectly clear solution with 4 parts of pure water. In dilution of 1 to 20 no precipitate must be formed with hydrogen sulphide, dilute sulphuric acid or barium chloride; nor must ferric chloride, potassium ferrocyanide or tannic acid produce either coloration or precipitate after acidulation with hydrochloric acid. On

evaporation with nitric acid no brown tint nor empyreumatic odor should appear.

PREPARATION. When pure ammonium chloride cannot be obtained, the best commercial article may be purified either by careful resublimation, or by making a saturated solution in boiling water, adding to this a little chlorine water, so as to convert ferrous salts into ferric, and then adding a slight excess of ammonia water, so as to precipitate ferric hydrate. The liquid is heated to expel all the excess of ammonia, the precipitate is separated by filtration and the filtrate set aside to crystallize, being occasionally stirred to prevent the formation of large crystals. The crystals are drained on a funnel; if not yet entirely pure they are recrystallized; 1 part of the dry salt is dissolved, for ordinary use, in 8 parts of pure water.

A volumetric solution of *five-times-normal ammonium chloride*, made by dissolving 266.96 grammes of the pure dry salt in water and diluting so as to fill 1 litre, is used in water analysis for the separation of calcium from magnesium.

AMMONIUM CITRATE, $(NH_4)_3C_6H_5O_7$.

USES. In the analysis of phosphates and phosphatic fertilizers, solutions of ammonium citrate are used in two degrees of concentration.

There are 3 varieties of calcium phosphate, the primary, $CaH_4(PO_4)_2$, also called the acid or monobasic, soluble in water; then the secondary, $CaHPO_4$, also called the dibasic or neutral (the so-called "reduced" phosphate, which is insoluble in water, but soluble in solution of ammonium citrate; the third is the tertiary, $Ca_3(PO_4)_2$, also called tribasic, which is insoluble in either water or ammonium citrate. Mol. W. = 188.564.

PREPARATION. For the concentrated solution, 100 grammes of pure citric acid are dissolved in a mixture of 100 Cc. pure water and 120 Cc. ammonia water of 10%. The solution is then accurately neutralized by addition of ammonia water, poured into a 1 litre flask and filled up to the mark with water.

The dilute solution for washing is made by diluting 1 part of the concentrated solution with 2 parts of water.

Ammonium-magnesium citrate solution is sometimes used for the precipitation of phosphoric acid, and is prepared as follows: 27 grammes pure magnesium carbonate are added gradually to a hot solution of 270 gr. citric acid in 350 Cc. water; after solution, 400 Cc. ammonia water of 10% are added, and the mixture filled up with water to 1 litre.

AMMONIUM FLUO-BORIDE OR BORO-FLUORIDE, $NH_4F . BF_3$.

USES. Ammonium or sodium boro-fluoride, which are quite soluble in water, form, on adding them to potassium salts, precipitates of potassium boro-fluoride, requiring 223 parts of cold water for their solution; soluble in 16 parts of boiling water (Stolba).

TESTS. No precipitate should be produced by hydrogen sulphide or ammonium sulphide. As the reagent is only used for qualitative work, the presence of some silico-fluoride and borate is not objectionable.

PREPARATION. The first step is the preparation of *hydro-fluoboric acid*, by heating 1 part of powdered boric anhydride, obtained by fusing boracic acid (or instead thereof 2 parts of powdered borax glass) with 2 parts of finely powdered fluorspar and twelve parts of concentrated sulphuric acid.

Boron trifluoride, BF_3, is formed, a colorless gas, fuming in air, which is conducted by a glass tube into 10 parts of distilled water, in which it readily dissolves, forming a dense solution, intensely acid, containing boric and hydro-fluo-boric acid.

This is carefully saturated with strong ammonia water (or, if the sodium salt is required, with the sodium carbonate).

AMMONIUM HYDROGEN FLUORIDE, $NH_4F . HF$.

USES. For the decomposition of silicates, titanates, tin stone, chromic iron ore, etc., instead of hydrofluoric acid or potassium hydrogen fluoride (*Gibbs*).

TESTS. Neither hydrogen sulphide, ammonium sulphide, ammonia, ammonium carbonate, nor sodium phosphate with ammonia should produce a precipitate. No residue must be left on evaporation.

PREPARATION. In a platinum vessel pure hydrofluoric acid is supersaturated with ammonia and carefully evaporated. Hydrofluo-silicic acid can also be used, the precipitate being separated by passing through a filter previously washed out with hydrofluoric acid. Commercial salt may be purified by precipitating and filtering just like hydro-fluo-silicic acid. It is best to prepare the reagent only in sufficient quantity for present use, as it must be preserved in guttapercha vessels, and, if kept in glass, attacks it, becomes contaminated and must be purified.

AMMONIUM HYPOSULPHITE, $(NH_4)_2S_2O_3$.

Ammonium Thio-Sulphate.

USES. Ammonium hyposulphite has been proposed (as well as other hyposulphites) to serve as a general reagent, instead of hydro-

gen sulphide, for separating metals into analytical groups; also as a special reagent for separation of cadmium from copper (*Orlowski*). From solutions acidulated with H Cl it precipitates the same metals as H_2S, excepting lead, tin, antimony and cadmium.

TESTS. Ammonium hyposulphite forms colorless, deliquescent crystals, which must volatilize at high heat without residue. Silver nitrate produces in its solution a white precipitate, turning black after awhile, or immediately on application of heat. Hydrochloric acid, added to solution, leaves it clear at first, but soon, especially on heating, precipitates sulphur, while sulphur dioxide escapes.

PREPARATION. In milk of lime, made by mixing 100 parts of freshly slaked lime in fine powder with 500 parts of water, 90 parts of sulphur are boiled for some time, replacing the water as it evaporates. The solution after cooling is decanted, and saturated with sulphur dioxide gas, until the yellow color disappears and sulphur is no longer precipitated. It is then filtered and a concentrated solution of ammonium carbonate is added as long as calcium carbonate precipitates. The liquid is filtered, concentrated by evaporation on water bath, and set aside to crystallize. The crystals are purified by recrystallization, and 1 part is dissolved for use in 5 parts of water. In nearly all cases, sodium hyposulphite may be used instead of the ammonium salt.

AMMONIUM META-VANADATE, NH_4VO_3.

USES. When dissolved in sulphuric acid, ammonium meta-vanadate serves to detect a number of alkaloids by very characteristic color reactions—colchicin, blue-green; gelsemine, purple; hydrastine, carmine red; narcotine, vermilion; piperine, blood red, then black; strychnine, violet-blue, changing to red; etc., etc. (*Mandelin.*)

TESTS. Absence of nitric acid must be shown by any of the various tests. Absence of chromium is shown by dissolving in dilute hydrochloric acid and adding hydrogen dioxide, freshly prepared from barium dioxide and dilute hydrochloric acid. Pure vanadates produce a red color, not communicated to ether, which remains colorless when shaken with it, while the presence of chromates is revealed by a blue color, communicated to ether. Absence of lead is shown by H_2S in acid solution, that of iron by potassium ferrocyanide or other tests.

PREPARATION. Lead vanadate or other rich vanadium ores are finely powdered, mixed with saltpetre and fused. The melted mass of impure potassium vanadate is dissolved in water, filtered, neutralized by nitric acid and precipitated by barium chloride. The

impure barium vandate is washed and then decomposed with dilute sulphuric acid. The barium (and lead) sulphate is removed by filtration, the filtrate is neutralized with ammonia water, and then concentrated by evaporation. A solid piece of ammonium chloride is placed into the solution, which gradually dissolves, and thereby separates from it granules of white ammonium meta-vanadate. The salt is washed with concentrated solution of ammonium chloride, in which it is insoluble; it is then dried and, if necessary, purified by recrystallization. For use 1 part is dissolved in 200 parts of pure sulphuric acid of spec. gr. 1.77, and preserved in glass-stoppered vials.

Ammonium Molybdate, see *molybdic acid, c.*

AMMONIUM NITRATE, $N\,H_4\,N\,O_3$.

USES. In dry substance, to oxidize metals, carbon, etc., to facilitate the combustion of filters; also in solution in the molybdate proc ss for determining phosphoric acid. Mol. W. = 79.922.

TESTS. No residue must be left on heating upon platinum foil. No precipitate in watery solution, acidulated with nitric acid, by silver nitrate, nor by barium chloride.

PREPARATION. Pure ammonium carbonate is saturated with pure nitric acid, and heated to expel carbon dioxide; then some ammonia water is added to alkaline reaction, and the clear solution set aside to crystallize. The crystals are dried, fused in a platinum dish, and preserved in glass-stoppered bottles.

AMMONIUM OXALATE $(N\,H_4)_2\,C_2\,O_4 + H_2\,O$.

USES. To precipitate the salts of metals, especially those of calcium; to separate calcium, barium, zinc and lead, which form insoluble oxalates from vanadic acid, which remains in solution (*Halberstadt*); to separate calcium from strontium by a solution containing 30 gr. ammonium oxalate and 200 gr. ammonium sulphate in 1 litre of water (*Sidersky*). Mol. W. = 141.78.

TESTS. The salt on ignition upon platinum foil must volatilize completely. No precipitate must be formed in its solution by hydrogen sulphide or ammonium sulphide. The precipitates by barium chloride and by silver nitrate must completely redissolve in nitric acid.

PREPARATION. The solution may be made by dissolving 1 part of pure oxalic acid in 21 parts of water, adding 4 parts of ammonia water of 10%, and heating long enough to expel the excess of ammonia. If much water is lost by evaporation it must be restored, so as to make 25 parts of solution, as ammonium oxalate is not soluble in a less quantity of water.

The crystals are prepared by supersaturating a hot saturated solution of pure oxalic acid in water with strong ammonia water, boiling to expel excess of ammonia and setting aside to crystallize. 1 part of the crystals is dissolved in 24 parts of pure water.

Volumetric solution of ammonium oxalate for titration of aluminium salts, etc., contains for deci-normal strength 14.2 gr. crystallized ammonium oxalate in 1 litre. Calcium chloride serves as indicator.

AMMONIUM PHOSPHATE, $(NH_4)_3PO_4 + 3H_2O$.

USES. For precipitation of magnesia, when the introduction of sodium phosphate is to be avoided on account of subsequent search after alkalies.

TESTS. Absence of metals is shown by precipitating from the aqueous solution all the phosphoric acid by lead acetate, removing any excess of lead by hydrogen sulphide and evaporating the filtered solution. No residue must be left on heating upon platinum foil. Absence of arsenic is to be proved by Fleitmann's test (see nitric acid, page 14); absence of sulphates by barium chloride after acidulation with nitric acid.

PREPARATION. Fifteen Cc. of pure phosphoric acid, of spec. grav. 1.347 (U. S. P. strength), are slightly supersaturated with ammonia water, and then diluted with distilled water to 100 Cc. The dry salt is obtained by saturating pure phosphoric acid with strong ammonia water, evaporating until it begins to solidify, mixing again with a slight excess of strong ammonia water and setting aside to crystallize. The crystals must be preserved in well-closed bottles, as they lose ammonia and gradually form the secondary salt, $(NH_4)_2HPO_4$. One part is dissolved for use in 10 parts of pure water.

AMMONIUM SELENITE, $(NH_4)_2SeO_3$.

USES. Selenous, as well as selenic acid, or rather the solutions of their alkali salts in sulphuric acid, have recently been used in the analysis of alkaloids, etc. Elaterin, colocynthin and hydrastine give peculiar color reactions (Johannson); codeine produces, even in minimal quantities, a green color (*Lafon*), etc.

PREPARATION. Powdered selenium is dissolved in concentrated nitric acid, which oxidizes it to selenous acid, H_2SeO_3. The solution is evaporated to dryness, and the acid may be thus preserved or dissolved in water, saturated with ammonia and crystallized. Both the acid and the ammonium salt must be carefully protected from light and contact with reducents. See also *sodium selenate*.

AMMONIUM SUCCINATE, $(NH_4)_2C_4H_4O_4$.

USES. In quantitative analysis, to separate ferric and aluminium salts as insoluble succinates from zinc, manganous, nickelous and cobaltous salts, whose succinates are soluble.

TESTS. The salt crystallizes in long, colorless, triclinic prisms, which, by long keeping, lose ammonia, forming the acid salt. It must leave no residue on heating upon platinum foil. A concentrated solution, when mixed with concentrated potassium acetate and some acetic acid, should not yield a precipitate of cream of tartar (absence of tartaric acid). After acidulation with nitric acid, neither silver nitrate nor barium chloride should produce a precipitate. When heated with indigo solution and sulphuric acid it should not discharge the blue color.

PREPARATION. The crude acid, of which about 4 per cent are obtained by the dry distillation of amber, is freed from oil by solution in hot water, filtration, concentration and crystallization. After recrystallization, the acid is dissolved in dilute nitric acid, heated and repeatedly recrystallized until a white product free from empyreuma is obtained. Care must be taken to wash the crystals so as to remove nitric acid. It is then supersaturated with ammonia water, crystallized (and recrystallized, if necessary) and the dry salt preserved for use in well-closed bottles to prevent loss of ammonia. For use, 1 part is dissolved in 10 parts of water, rendered slightly alkaline by ammonia.

AMMONIUM SULPHATE, $(NH_4)_2SO_4$.

USES. To introduce sulphuric acid without disturbing the neutrality, as in precipitating barium, etc. To separate, in conjunction with ammonium oxalate, calcium from strontium. To precipitate urates and albumoses in urine.

TESTS. Ammonium sulphate forms colorless, rhombic crystals, soluble in two parts of cold water. It should be completely volatilized by heat, decomposing into ammonia, free nitrogen, water and ammonium sulphite, which sublimes. As the commercial salt is difficult to purify, it is best to make it from pure materials.

PREPARATION. Pure dilute sulphuric acid is fully saturated by gradual addition of ammonia water. The neutral solution is evaporated and crystallized.

AMMONIUM SULPH-HYDRATE, NH_4HS; AMMONIUM SULPHIDE $(NH_4)_2S$; AND AMMONIUM POLYSULPHIDE, $(NH_4)_2S_x$.

USES. Ammonium sulphide and sulph-hydrate are generally employed either indiscriminately or in a mixture containing vari-

able quantities of both. They serve to precipitate the metals of the third (or aluminum) group as hydrates, and those of the fourth (or iron) group as sulphides.

Mixed with the yellow polysulphide they are used to separate the sulphides of the sixth (or arsenic) group, which dissolve from those of the fifth (or copper) group, which are insoluble in ammonium sulphide; also in organic analysis, e. g., to recognize chloral hydrate by a characteristic precipitate. Occasionally an alcoholic solution is substituted for the aqueous one.

TESTS. Ammonium sulphide and sulph-hydrate must not contain ammonium carbonate or free ammonia; hence, solutions of calcium or magnesium salts must not be rendered turbid by them, even when heated. They must be perfectly volatilized on heating. Hydrochloric acid should not produce any precipitate in the colorless sulphide or sulph-hydrate, and only a white precipitate of pure sulphur in the yellow polysulphide. Purity is best insured by using for their preparation pure materials, careful washing of the gas and full saturation.

PREPARATION. Hydrogen sulphide, made as directed in the article treating of that reagent, (H_2S, page 10), is passed through a wash-bottle and into a bottle containing pure 10% ammonia water until it ceases to be absorbed. The liquid consists now of a solution of ammonium sulph-hydrate. This may be preserved and used as it is, but generally it is converted, at least partially, into sulphide by the addition of more ammonia water. If this be added in too large a quantity, or if the saturation at first was incomplete, free ammonia will be present in the mixture, which would lead to errors in analysis. Hence, it is best to use only enough ammonia water to partially convert the sulph-hydrate. Theory requires exactly the same amount of ammonia to be added as that which was first taken for saturating with the gas. Usually, 3 volumes of the sulph-hydrate are mixed with 2 volumes of ammonia water of the same strength as that used at first.

The colorless product should be preserved in small bottles, well protected from air and light, for exposure decomposes it and renders it yellow.

At first, only a polysulphide is formed, but soon more oxygen is absorbed and polythionates form, which render its use objectionable.

To make the yellow polysulphide, pure sulphur should be digested with the above solution of sulphide, and the clear liquid decanted from undissolved sulphur and well preserved.

AMMONIUM SULPHOCYANATE, NH_4CNS.

(*Sulphocyanide, Thiocyanate or Rhodanate.*)

USES. The soluble sulphocyanates, especially the potassium and ammonium salt, are used to detect ferric salts, and distinguish them by their intense red color from the colorless ferrous. Also to precipitate from cupric salts in presence of a reducent, such as SO_2, white cuprous rhodanate. Also in the volumetric silver assay by *Volhard's* process.

Presence of calcium, strontium, barium, magnesium and some other chlorides interferes with the ferric reaction, and in small quanties prevents it entirely. Mol. W. = 76.0.

TESTS. The watery solution must remain clear and colorless on addition of hydrochloric acid. With silver nitrate it must form a pure white precipitate completely soluble in ammonia water.

PREPARATION. To 4 parts of pure carbon disulphide add 15 parts each of strong alcohol and concentrated ammonia water. Mix well, and leave them to digest for several days. Two-thirds of the mixture are then removed by distillation; the remaining third is filtered, concentrated and at last set aside to crystallize, under a bell glass, over sulphuric acid. Colorless, very deliquescent crystals will form, which must be purified by recrystallization. In all these operations, too high a temperature must be avoided, otherwise the salt will decompose, forming thio-urea, etc.

Another mode of preparation consists in digesting a mixture of hydrocyanic acid and yellow ammonium polysulphide, the latter being in some excess. After some days standing, the excess of ammonium sulphide is removed by heat, and the crystals are obtained as in the other method. They must be preserved in well-closed bottles, as they rapidly attract moisture from the air and dissolve in four-fifths of their weight of water.

Decinormal Solution is made by dissolving eight grammes of the salt in one litre of water, and diluting, so as to correspond accurately with decinormal solution of silver nitrate. A 10% solution of ferric alum is used as indicator.

ANILINE COMPOUNDS.

ANILINE, $C_6H_5NH_2$.

Amido-Benzol

USES. Aniline, dissolved in alcohol, is used to detect chloroform, chloral, etc., by the production of the characteristic isonitril odor,

when heated together with them and a solution of an alkaline hydrate (*Hoffman*). A solution of 0.5 Cc. of pure colorless aniline in 15 Cc. of alcohol and 15 Cc. of concentrated ether, is used to detect minute quantities of fluorine in silicates by passing through it the vapor evolved when the silicate is heated with sulphuric acid. Aniline silicofluoride is formed, and afterward converted into sodium silicofluoride by addition of sodium hydrate dissolved in absolute alcohol (*Knop*).

A mixture of 1 Cc. of colorless aniline oil with 0.5 Cc. of hydrochloric acid forms *Jorissen's* test for furfurol in fermented and distilled liquids. This quantity is added to ten Cc. of the alcohol, whiskey, etc., to be tested, and shows the presence of furfurol, $C_5H_4O_2$ (pyromucic aldehyde), by a rosered color.

In saturated aqueous solution, aniline serves to dissolve gentiana violet, fuchsin, etc., for the staining of micro-organisms. Also used in the preparation of aniline sulphate, hydrochlorate and other salts and derivatives.

Filter paper, saturated with aniline oil, neutralized with hydrochloric acid, indicates ozone in gas mixtures by assuming a brown color (*Wagner*). The browning of colorless aniline oil under influence of air and light is attributed by Schoenbein to ozone, but is not as sensitive a test as the hydrochlorate.

It is also used in gas analysis in the place of glacial acetic acid, as an absorbent of cyanogen in mixtures of gases (*Jacquemin*).

Also for the volumetric determination of nitrous acid, based upon the formation of di-azo-benzol (*Green and Rideal*). Mol. W — 92.865.

TESTS. For most purposes the commercial *aniline oil* is sufficiently pure, when recently distilled and colorless; for making the sulphate for the nitric acid test it is even preferable on account of containing para-toluidine. Pure aniline is a colorless liquid of spec gr. 1.0276 at 12° C. It dissolves in 31 parts of water at 12.5° C., is miscible with alcohol in all proportions. Its reaction is feebly alkaline, discernible by dahlia paper, but not by litmus. With sodium hypochlorite in dilute solution it gives a purple violet color. It must be proven free from arsenic by Fleitman's test.

PREPARATION. On the large scale, aniline is made by reducing nitro-benzol with nascent hydrogen from iron chips and hydrochloric acid, then adding lime and distilling. When absolutely pure materials are used this furnishes pure aniline. But when the nitro-benzol has been made from impure benzol, or when arsenic trioxide has been used in the manufacture, the crude oil must be purified. The removai of ortho-toluidine is accomplished by saturating the aniline oil with hydrochloric acid, then adding sodium phosphate to decompose the salt. The mixture is kept warm and

separates into two layers; the lighter, containing the oily ortho-toluidine, is removed, and the heavier residue is set aside to cool, when crystals of aniline, and para-toluidine phosphate are formed. These are purified by recrystallization, then decomposed by sodium hydrate and distilling (L. Levy). The distillate is reduced to the temperature of 10° C., when most of the paratoluidine crystallizes, its melting point being 45° C., while aniline remains liquid down to 8° C. The liquid aniline is separated by filtration, and may be further purified by fractional distillation, preserving the fraction, coming over at 182.5° to 184° C.

Perfectly pure aniline may be made, on a smaller scale, by using pure acetanilide (*antifebrine*), which is easily purified by recrystallization from benzol and by distillation at 295° C. The pure acetanilide is decomposed by sodium hydrate and the aniline distilled off and rectified by redistillation.

Decinormal Solution for the analysis of nitrites is made by mixing 9.3 grammes of pure aniline oil with 100 Cc. of normal sulphuric acid and 100 Cc. normal hydrochloric acid, and filling up to 1 litre with distilled water. Starch solution, with potassium iodide, is used as indicator. A *normal solution* is more recently used containing 93 gr. aniline and 450 Cc. hydrochloric acid in 1 litre.

ANILINE SULPHATE, $(C_6H_5NH_2)_2H_2SO_4$.

USES. Aniline sulphate, containing para-toluidine sulphate, is used in solution in strong sulphuric acid to discover small traces of nitrates (in drinking water) by the production of an intense red color. Pure aniline sulphate hardly shows the reaction, but when mixed with paratoluidine the reaction is more distinct than with either reagent alone. Nitrites, in concentrated solution, produce with it a yellowish brown; in dilute solutions, a faint yellow color, due to the formation of diazobenzol. With chlorates, bromates, iodates and hypochlorites violet to blue colors are produced, with chromates, permanganates and vanadates, orange changing to violet.

Aniline sulphate forms a valuable reagent for recognition of wood pulp in paper, as it colors the lignin a golden yellow, while pure cellulose remains unaffected.

A decinormal solution containing 14.2 gr. aniline sulphate and 3.65 gr. hydrochloric acid in 1 litre has been proposed for the titration of nitrites (*Green & Rideal*), but is little used on account of the difficulty of avoiding sources of error.

TESTS. Aniline sulphate is readily soluble in water and acids, less in strong alcohol, insoluble in ether. Its solution colors pine

wood intensely yellow, produces with hypochlorites a violet color, with solution of potassium dichromate and sulphuric acid, first an orange then a blue. The commercial salt is sufficiently pure.

PREPARATION. For most purposes a solution of 1 part aniline oil in 99 parts of concentrated sulphuric acid answers best.

p AMIDO.DIMETHYL-ANILINE, $C_6 H_4 . N H_2 N (C H_3)_2$.

Dimethyl-para-phenylen-diamine.

USES. In conjunction with ferric chloride and hydrochloric acid, to detect, by the production of *methylene blue*, even such minute traces of hydrogen sulphide as would escape detection by lead salts or other reagents (*Caro and Fischer*). To about 50 volumes of the aqueous solution, suspected of containing $H_2 S$, one volume of concentrated hydrochloric acid is added, and then a few granules of para-amido-dimethyl-aniline, or its sulphate or hydrochlorate. After solution, a drop or two of dilute solution of ferric chloride is added. If hydrogen sulphide was present the liquid, after a little time, assumes a deep blue color. The addition of hydrochloric acid is necessary to prevent the formation of the red coloring matter, which would interfere with the delicacy of the reaction.

Paper stained with a solution of this reagent, as well as with *tetra-methyl-paraphenylen-diamine*, has been introduced by *Wurster* as a delicate reagent for ozone. When moistened it turns blue with the smallest quantities of this active modification of oxygen. It also serves to detect substances which ozonize air, such as turpentine, colophony, etc. Hence, it is used to detect wood pulp in paper, during whose manufacture rosin is added to the pulp. A moist strip of *Wurster's paper* pressed upon such wood pulp paper turns blue.

PREPARATION. From Helianthin (Orange III) as described in article on preparation of *sulphanilic acid*, on page 21.

p Amido-benzol-azo-dimethyl-aniline, $N H_2 . C_6 H_4 . N{:}N. C_6 H_4 . N (C H_3)_2$. Used for the detection of nitrous acid, with which it forms a tetrazo salt, whose dilute solution turns blue on exposure to air (*Meldola*).

NOTE. For other derivatives of *Aniline* and its homologues, see the articles as they occur in alphabetical order, and especially those in the chapter on *Color Reagents and Indicators*.

ANTHRAQUINONE, $C_6 H_4 (C O)_2 C_6 H_4$.

USES. To detect the presence of small quantities of water in alcohol, etc. (*Claus*). A few milligrammes of anthraquinone and

sodium amalgam are mixed and thoroughly shaken up with absolute ether (being absolutely free from alcohol and moisture). A few drops of the liquid to be tested for water are then added. If water be present a red color is produced. Absolute alcohol (which may be added without ether being used) produces a green color. Both colors disappear on shaking with air, but reappear again on standing quietly.

TESTS. Anthraquinone forms yellow, rhombic, needle-shaped crystals, melting at 273° C. and subliming at a higher temperature without residue. The commercial article is produced on the large scale by oxidation of anthracene, as a step in the manufacture of artificial alizarine, and is sufficiently pure for the above reaction.

PREPARATION. On the small scale, it may be made by passing chlorine (or bromine) into a boiling solution of one part of anthracene in 6 parts of strong alcohol. After cooling, the precipitate is first washed on a filter with cold alcohol, then with dilute solution of sodium hydrate in water, then dried and sublimed in a glass tube.

ANTIPYRINE, $C_{11} H_{12} N_2 O$.

Dimethyl-oxy-chinizine.

USES. To detect free nitrous acid (in amyl nitrite, ethyl nitrite, etc.) by the production of a deep emerald green color. A solution of antipyrine in water is added to this substance. If free nitrous acid is present a deep green color at once results, followed by the deposition of green crystals of iso-nitroso-antipyrine, $C_{11} H_{11} N_3 O_2$. These are insoluble in water, soluble in alcohol, acetic acid and in alkaline hydrates. An excess of nitrous acid or nitric acid oxidizes the green salt and colors it red.

By using a mixture of strictly neutralized sodium nitrite and antipyrine solutions, the presence of any *free acid* capable of liberating nitrous acid may be detected by the same reaction.

With ferric salts antipyrine produces a red color similar to that of the sulphocyanides, but the reaction is not so delicate in great dilutions.

TESTS. Antipyrine, as sold by dealers, is sufficiently pure for use as a reagent. It forms a white crystalline powder, melting at 113° C., soluble in two-thirds its weight of water. The solution is neutral to test papers. When mixed with some potassium or sodium nitrite and a few drops of sulphuric acid it must promptly turn green. It must be carefully preserved in the dark, as exposure impairs its activity.

PREPARATION. The process of manufacture patented by Dr. Knorr consists in the production of methyl-oxy-chinizine, by the

condensation of equal molecules of phenyl-hydrazine and aceto-acetic ester. This is heated at 100 C. in closely sealed vessels with an equal amount of methyl alcohol and methyl iodide, and thus an impure icdide of the *dimethyl* compound results. This is purified by treatment with sulphur dioxide, and then the base is separated by sodium hydrate and purified by recrystallization from toluol, ether or benzol. The solution is only made when needed, and then 1 part of antipyrine is dissolved in ten parts of pure water.

ARSENIC TRIOXIDE, As_2O_3.

Arsenous Acid Anhydride.

Uses. Arsenic trioxide serves to detect acetic acid in presence of other volatile organic acids by the kakodyl test. When an alkaline acetate is fused with As_2O_3 the very characteristic, disagreeable odor of dimethyl-arsine (kakodyl) is produced. It is also occasionally used as a reducing agent to convert nitro-benzol into aniline, etc. Also for the preparation of decinormal volumetric solution of sodium arsenite, used in the titration of chlorine, hypochlorites, bromine, iodine, etc. For the latter purpose the arsenic trioxide must be very pure. Mol. W. = 122.798.

Tests. Pure arsenic trioxide must completely volatilize when heated in a glass tube; the sublimate it then gives must be perfectly colorless or white, and must not at first show a reddish color of the more easily sublimed sulphide, whose presence would render it unfit for volumetric use, as it rapidly changes the titre of the solution by the formation of arsenic acid. The solution in water must not be colored dark by lead solution (absence of sulphide). It must give with ammoniated solution of silver nitrate a pure yellow precipitate (a brown red precipitate would indicate presence of arsenic acid). Its aqueous solution, acidulated with pure hydrochloric acid, must give with hydrogen sulphide a pure yellow precipitate. When converted into arsenetted hydrogen in a Marsh apparatus, the spots produced by the ignited gas on porcelain must completely dissolve in sodium hypochlorite, showing the absence of antimony.

In the powdered arsenic of commerce, the absence of chlorides may be shown by converting the trioxide into arsenic acid by means of boiling with concentrated nitric acid, diluting and then adding silver nitrate, when a white precipitate, soluble in ammonia, will indicate chlorine.

Ammonium salts are said to be occasionally present, and may be detected by heating with sodium hydrate.

PREPARATION. From the white arsenic of commerce arsenic trioxide may generally be obtained of great purity by breaking open the larger pieces and carefully selecting the glassy transparent amorphous inner portions, rejecting the opaque, porcelain-like crystalline crust. The glassy amorphous modification is much more soluble in water than the crystalline opaque envelope. It is tested for purity, and, if found pure, is preserved in glass stoppered bottles. It will soon become covered by an opaque crust, but this will not interfere with its use when it has once been found pure.

ASBESTUS, AMIANTHUS.

USES. Asbestus is a natural silicate of calcium and magnesium, closely allied to hornblende; its purest variety is called amianthus. It occurs in slender, flax-like fibres, capable of resisting high temperatures without fusing, and is not attacked by water and most of the acids. This makes it valuable material for filtering many substances which would destroy ordinary filtering paper. It is also used to close tubes, etc., in such manner that gases can easily pass through its interstices while powdered solids are retained. Sometimes it is impregnated with concentrated sulphuric acid and placed into tubes to dry the passing gases. Occasionally it is coated with a finely divided metal, and thus used in either gas analysis or in the combustions of organic ultimate analysis. The long fibre is used as a support in blowpipe operations in the place of platinum wire. It is also woven into cloth, useful for various purposes.

TESTS. The purest variety, amianthus, is preferable for most purposes, whether requiring long or short fibre. It must not yield anything soluble to either hot or cold water or hydrochloric acid. After boiling for some time with concentrated hydrochloric acid, this, on evaporation upon platinum foil, must show no residue. It must resist the temperature of white heat without fusion.

PREPARATION. Asbestus of a less degree of purity may be used after having been deprived of all soluble matter by boiling with hydrochloric acid and thorough washing. *Palladium-asbestus* is made by dissolving 1 gramme of palladium in nitro-muriatic acid, and evaporating the solution until all free acid is expelled. The palladious chloride (about 1.7 gr.) is dissolved in very little water, and to this are added 5 Cc. of a cold, saturated, aqueous solution of sodium formate and enough pure sodium carbonate to render the liquid alkaline.

With this mixture one gramme of pure, long-fibred amianthus is impregnated and dried; first at a very gentle heat, lastly at 100 C.

The palladium, reduced to a fine metallic state, is precipitated upon the fibre, and after being perfectly dried adheres well. It is washed with warm water upon a funnel until all soluble salts are removed, then again dried at 100° C., and carefully preserved without bending or unnecessary handling, in glass tubes. It is used to absorb hydrogen from gas mixtures, etc.

Platinum-Asbestus is prepared in the same manner, using for 1 gramme of asbestus 1.2 gr. of platinic chloride, corresponding to about 0.5 gr. of metal.

Copper-Asbestus is made by impregnating the short-fibred variety with saturated solution of pure copper nitrate, drying and heating to redness, when the salt will be converted into black cupric oxide. It is then heated in a current of hydrogen gas until the oxide is fully reduced to metal. In the elementary analysis of organic substances containing nitrogen this is used instead of copper turnings.

NOTE. Many other silicates, natural and artificial, are employed for the same purposes as asbestus. Thus, pumice stone is used for soaking with sulphuric acid to dehydrate gases; it is also coated with metallic copper for organic analysis. Garnets, quartz in small fragments, kieselguhr, glass wool and slag wool are used for filtering acids.

ASSAY REAGENTS,

also called *docimastic* or *pyrognostic* reagents, are used in the assay of ores, etc., in the dry way, by blowpipe or furnace operations. They are described under their respective titles. See *Silicic Acid, Coal, Fluxes, Lead, Lead Monoxide, Sodium Diborate, etc.*

AZOLITMIN.

USES. Azolitmin, being the most important of the four coloring principles contained in litmus, is sometimes isolated to serve as indicator in alkalimetry and for the preparation of test papers. The removal of the other coloring principles, which interfere with its prompt reaction, makes it more sensitive than the crude litmus preparation. It is colored red by acids, blue by alkalies.

TESTS. Azolitmin forms an amorphous, red-brown powder, very little soluble in water, insoluble in acids, forming with alkalies blue salts, which easily dissolve in water.

PREPARATION. Litmus is digested with 6 parts of hot water; the solution is filtered, and into it strips of cotton or linen cloth (free from starch) are immersed until the color has been absorbed. They are then taken out, permitted to drip and, when partly dry, are immersed into dilute sulphuric acid (1%). The acid renders the

azolitmin red and insoluble, and fixes it in the fibre. The strips are next washed in water until no more coloring matter can be extracted. This removes the other pigments and leaves only azolitmin in the cloth. It is next soaked in water made alkaline by a small quantity of sodium hydrate. The blue, soluble sodium salt is formed, and may be extracted by pressure. From this solution either the dry azolitmin is obtained by precipitation with sulphuric acid, or the solution is mixed with only a few drops of very dilute acid to give it a neutral purple tint, and then preserved as an indicator for alkalimetric work, or converted into test paper by soaking strips of unsized paper with it. See also *Color Reagents and Indicators*, *Litmus and Testpapers*.

BARIUM COMPOUNDS.

BARIUM ACETATE, $Ba(C_2H_3O_2)_2 + H_2O$.

USES. To remove sulphuric acid by precipitation as barium sulphate in cases where the introduction of acetic acid is preferable to that of the other acids of barium salts. Hence, it is employed in the separation of magnesium from the alkalies (in water analysis, etc.). The sulphates of magnesium and the alkalies are converted into acetates, and these, by ignition, into carbonates. Water dissolves out the alkalies and leaves magnesium carbonate and oxide.

TESTS. As the reagent is but seldom used, it is best to prepare it, whenever needed, from pure materials. When bought in crystals it should, in addition to the tests used for other barium salts (see barium chloride), show the absence of hydrochloric, nitric and other acids. Its solution is therefore precipitated by dilute, pure sulphuric acid in slight excess and filtered. The filtrate must leave no residue when heated on platinum foil. It must give no precipitate with silver nitrate either before or after neutralization with sodium hydrate. With diphenyl-amine and concentrated sulphuric acid it must show no blue color.

PREPARATION. Pure barium carbonate is added in slight excess to pure dilute acetic acid. After standing some time, the solution is filtered and is then ready for use. By evaporation crystals may be obtained, which are dissolved in 7.2 parts of water, when needed in solution.

BARIUM CARBONATE, $BaCO_3$.

USES. Native barium carbonate, witherite, is too impure for analytical purposes, but is often used to prepare from it pure barium

chloride and other salts. The pure salt is used to remove by precipitation ferric, chromic and aluminium salts from those of zinc, manganese and other bases of the third and fourth analytical groups, sulphuric acid being absent. Also to remove sulphuric acid from solutions, etc. Also to prepare some of the less frequently used barium salts, such as the acetate, by saturating their acids.

TESTS. Barium carbonate must yield nothing to pure water deprived of carbonic acid gas by boiling. It must leave no residue insoluble in water after neutralization with pure dilute hydrochloric acid. On addition of a slight excess of pure dilute sulphuric acid to this solution, the whole of the base must be precipitated as barium sulphate, and after boiling and careful filtration, so that none of the fine particles of the precipitate can pass through the filter, addition of alcohol must not produce a turbidity (absence of calcium and strontium), nor leave any residue on heating upon platinum foil.

PREPARATION. To a boiling solution of pure, crystallized barium chloride in pure water add a concentrated solution of pure ammonium carbonate, mixed with a little ammonia water, as long as a precipitate falls. Wash out, first by repeated decantation, then on a filter, until every trace of chloride is removed, as shown by nitrate of silver. The precipitate is then dried and preserved free from dust, etc. For use it is mixed with pure water to the consistence of thick milk.

BARIUM CHLORIDE, $Ba\,Cl_2 + 2H_2\,O$.

USES. To detect and separate the inorganic acids of the first group, which form barium salts insoluble in water, from those of the other groups forming soluble barium salts. As a special reagent for sulphuric acid, whose barium salt is insoluble in water and in all dilute acids, but soluble in hot concentrated sulphuric acid as barium disulphate, $Ba\,(H\,S\,O_4)_2$. Also in volumetric analysis as normal and decinormal solution. $Ba\,Cl_2 + 2H_2\,O = 243.423$.

TESTS. The pure salt forms colorless, rhombic crystals, soluble in 2.3 parts of water at 15° C., insoluble in absolute alcohol, and in concentrated H Cl. The aqueous solution must be strictly neutral to test papers; must not yield any precipitate with hydrogen sulphide, or ammonium sulphide, containing no free ammonia. After precipitation with sulphuric acid in slight excess the filtrate must yield no precipitate with sodium carbonate and hydrate, nor leave any permanent residue on heating upon platinum foil.

To the flame it must communicate a yellowish-green color, free from red, showing a pure barium spectrum. To render the flame

test more effective, the salt is washed with alcohol of spec. gr. 0.928 and the washings tested, in which very little barium chloride dissolves, while the calcium and strontium salts, if present, are freely dissolved and thus more readily shown.

PREPARATION. There are two native minerals which serve as the source of barium preparations, the sulphate, called heavy spar or barytes, and the carbonate or witherite. On the larger scale, finely powdered barium sulphate is heated to a white heat with charcoal and manganous chloride (obtained as a bye-product in the chlorine manufacture). Or by heating together 12 parts of heavy spar, 6 parts of dry calcium chloride, 2 parts of charcoal and 2 parts of iron. The product in each case is leached out with boiling water, crystallized and refined by recrystallization.

On the smaller scale, 8 parts of finely powdered barium sulphate are mixed thoroughly with two parts of lampblack, and one part of linseed oil (or rosin), placed in a crucible and gradually heated up to a bright white heat, at which they are kept for many hours. The product, consisting of impure barium sulphide, is leached out with about four times its weight of water. Of the solution about 1-20th part is set aside, and to the rest a slight excess of hydrochloric acid is added. After the expulsion of the H_2S, the liquid is filtered, evaporated to about one-third, and then enough of the reserved barium sulphide solution is added to render the liquid slightly alkaline. It is now again filtered, evaporated to dryness, dissolved in three parts of water, filtered and, after slight acidulation with hydrochloric acid, concentrated and crystallized. The crystals are dissolved in 2 parts of hot water and 2 parts of alcohol added. This precipitates barium chloride, which is separated on a filter and washed with alcohol, while strontium and calcium chlorides remain in solution.

From witherite, barium chloride is made by dissolving 10 parts of the powdered material in about 15 parts of hydrochloric acid. After solution, 1 more part of witherite is added and digested in a warm place for 24 hours. In case iron is present, as shown by tannic acid and other reagents, enough of the solution of bleaching powder (calcium hypochlorite) is added to remove it. The liquid is then filtered, evaporated, crystallized, and after recrystallization, purified by precipitating with alcohol as above.

For use, 1 part of the crystals is dissolved in ten parts of water.

Normal solution contains 243.423 grammes in 1 litre.

BARIUM DIOXIDE, BaO_2.

USES. To prepare hydrogen dioxide for detection of chromic acid, titanic acid, etc.

TESTS. After precipitation by sulphuric acid the filtrate must on evaporation leave no fixed residue. When a small quantity is suspended in cold water and dilute hydrochloric acid added, it must yield sufficient hydrogen dioxide to color blue a dilute solution of potassium dichromate.

PREPARATION. As pure dioxide is somewhat difficult to obtain entirely free from oxide, and as the presence of this does not interfere with the use, a preparation of sufficient purity is obtained by heating dry barium oxide, Ba O, to a red heat in a suitable tube, while a current of oxygen is passing over it.

BARIUM HYDRATE, $Ba(OH)_2$.

(Crystallized: $Ba(OH)_2 + 8H_2O$.)

USES. In the dry state it is used as a flux to decompose silicates for the determination of their alkalies. In crystals and in solution it serves to remove CO_2 from mixed gases; to prepare pure alkaline hydrates; to liberate organic and inorganic bases from their compounds, e. g., glycerin from fats; to remove chlorophyll, etc. To precipitate acids forming insoluble barium salts, e. g., to remove sulphates, phosphates, etc., from urine, preparatory to testing for urea, etc. In volumetric analysis for acidimetry, determination of chloral hydrate, etc. Molec. weight: $Ba(OH)_2 = 170.683$; $Ba(OH)_2 + 8H_2O = 314.363$.

TESTS. After precipitation by sulphuric acid the filtrate must leave no fixed residue on evaporation. The salt $Ba(OH)_2 + 8H_2O$ is soluble at 15° C. in 20 parts of water, at 100° C. in 3 parts.

PREPARATION. Either by precipitation of a concentrated solution of barium chloride by sodium hydrate, or by heating barium nitrate for some time to a white heat and then adding water. Or better, by heating a mixture of 10 parts of barium carbonate with 1 part of lampblack, and 1 part of linseed oil (or rosin) for several days to a white heat (by placing the crucible in a brick kiln). The cooled mass is leached out with boiling water, filtered while hot, and the clear solution left to cool in well-stoppered bottles, so as to let the crystals deposit. They are separated by filtration and kept in well-closed bottles. In all of these operations access of air must be prevented as much as possible, so as to exclude its CO_2 from the solution, which would rapidly absorb it. From the crystals, the dry barium hydrate is obtained by heating them in a platinum or silver vessel till the water of crystallization is expelled, which occurs below a red heat.

Baryta Water. For use, 1 part of the crystals is dissolved in 20 parts of water, boiled immediately before, so as to expel CO_2. The

volumetric solution is made of *half-normal* strength, 157.181 grammes to 1 litre, containing 85.341 gr. of $Ba(OH)_2$. To prevent its rapid deterioration a special absorption tube is attached to the bottle, a layer of petroleum is poured upon its surface, and frequently the burette is connected with the containing vessel so as to exclude CO_2.

BARIUM MERCURIC IODIDE, $BaI_2 HgI_2$.

Rohrbach's Solution.

USES. In petrographic work the concentrated solution is used to separate various components of rocks by difference in specific gravity. The solution in its utmost concentration contains an excess of mercuric iodide and attains the spec. grav. 3.588, but becomes gradually lighter by the separation of crystals of mercuric iodide. Epidote and olivine float in it.

PREPARATION. Into a small flask place 100 grammes barium iodide (which may be made from barium carbonate and hydriodic acid), 130 gr. red mercuric iodide and 20 Cc. of water. Heat to 200° C. on an oil bath, accelerating the solution by agitation. As soon as dissolved, reduce the temperature to 100° and evaporate (in a porcelain dish) until a crystal of epidote floats. On cooling, the density increases. The solution is carefully decanted and preserved in a glass-stoppered vial.

For other petrographic reagents, see *Bromoform, Cadmium Borotungstate* and *Mercuric Potassium Iodide.*

BARIUM NITRATE, $Ba(NO_3)_2$.

USES. For the same purposes as barium chloride, when the introduction of chlorine is objectionable. By ignition it loses its acid and is converted into BaO. Mol. W. = 260.565.

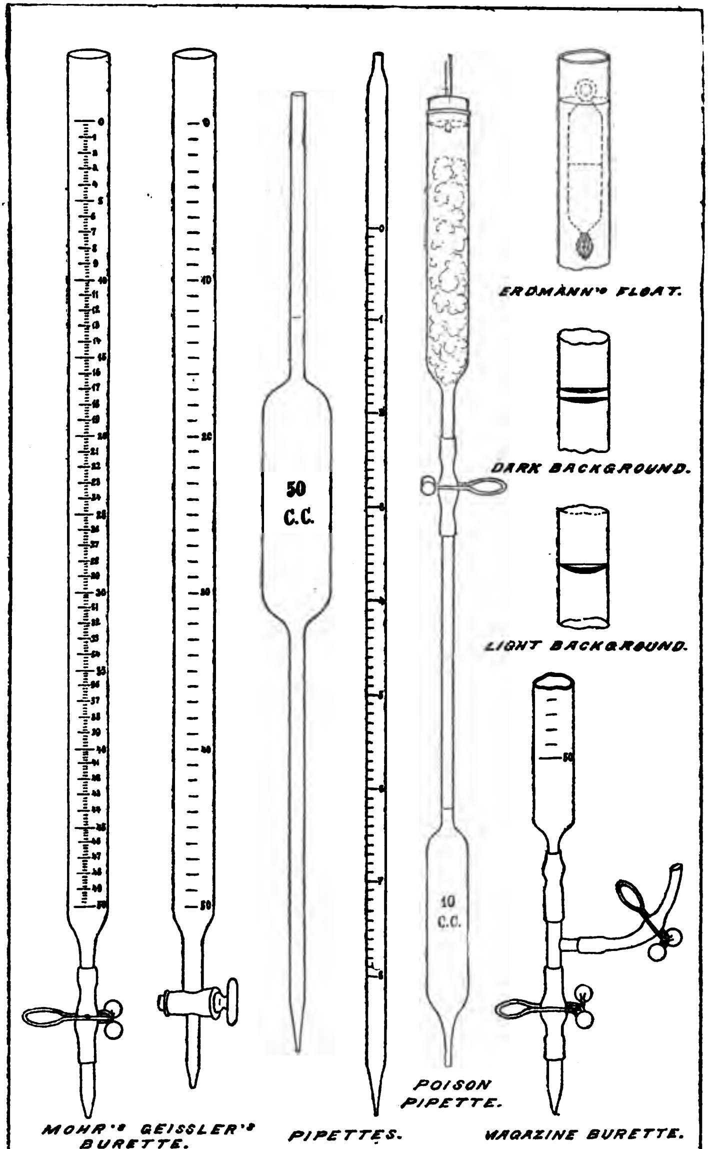
TESTS. It crystallizes in regular octahedra, soluble in 12 parts of water, insoluble in alcohol. In addition to the tests for other barium salts, the absence of chlorine must be shown by silver nitrate failing to give a precipitate in a dilute solution, slightly acidulated with nitric acid.

PREPARATION. Barium carbonate is saturated with dilute nitric acid, concentrated and crystallized.

For use, dissolve 1 part in 15 parts of water.

BARIUM SULPHIDE, BaS.

USED for the convenient preparation of *hydrogen sulphide free from arsenic* (Winkler). The almost universal freedom from arsenic of the native barium sulphate, from which the material is prepared, together with its cheapness, recommends it as a substitute



Charlotte S. Cushman Del.

for ferrous sulphide. It is used, broken into lumps, in any form of generating apparatus, and with pure acid furnishes pure hydrogen sulphide.

PREPARATION. 100 parts of heavy spar, 25 parts of powdered charcoal and 20 parts of sodium chloride are intimately mixed, and by aid of a little water formed into a stiff dough. This is pressed into clay crucibles of suitable size (about 25 Cm. high and 10 Cm. wide), and dried at a gentle heat. The crucibles are covered first with powdered charcoal, then the cover is luted on with clay, leaving a small opening for escape of gas. They are then heated for several hours to a white heat (in a brick kiln or suitable furnace). After cooling, the crucibles are easily emptied, the sintered mass broken into lumps of suitable size and preserved in tightly sealed cans. When stone coal, absolutely free from arsenical pyrites, is used in the place of charcoal, a more compact mass is obtained.

BENZIN.

Petroleum-ether.

NOTE. The volatile fraction of petroleum boiling between 50° and 60° C., of spec. gr. 0.670 to 0.675, consisting principally of pentane, C_5H_{12}, hexane, C_6H_{14}, and their isomers, is recognized in the U. S. P. under this name, while other authorities use the name for a different substance. The similarity of the name of the coaltar product, benzol, also called benzene, has led to some confusion. Dragendorff, who introduced the petroleum product into plant analysis, calls it *petroleum-ether*, including in this designation all the more volatile constituents, while he gives the name *benzin* to the coaltar derivative benzol, C_6H_6. To prevent mistakes it is best to follow the nomenclature of the Pharmacopœia, avoid the name benzene, and call the coaltar product BENZOL, as proposed by Liebig in 1834), confining the names BENZIN and PETROLEUM-ETHER to the more volatile portion of petroleum, although, strictly speaking, it is no ether.

USES. In organic analysis benzin is used for dissolving resins, oils and fats; the more volatile portions serve to remove the active principles of plants from various solutions. Thus, from acidulated solution petroleum-ether extracts salicylic acid, phenols, absinthin, piperine, lupuline, cantharidin, etc.; from alkaline solution strychnine, brucine, emetine, coniine, nicotine, etc., etc. (*Dragendorff.*)

TESTS. For solution of oils and fats the U. S. P. benzin is suitable. On evaporation, it should not leave a disagreeable odor of sulphur compounds, nor any less volatile residue, boiling above 60° C. On

agitating 2 parts of benzin with a mixture of four parts of nitric and one part of concentrated sulphuric acid, neither a dark color nor a bitter almond ódor should be produced, the latter indicating presence of benzol, which occurs in small quantity in Russian petroleum. For extracting alkaloids, etc., a petroleum-ether of lower boiling point is preferable.

PREPARATION. A sufficiently pure product, rectified on the large scale, is generally obtainable in the market. If necessary, commercial benzin may be refined by first digesting with a solution of potassium dichromate and sulphuric acid, washing and then mixing with about one-fourth of pure hogs lard. The mixture is carefully distilled, rejecting the portion boiling above 60° C., and, if necessary, redistilled.

BENZOL, C_6H_6.

(*Benzene.*)

USES. As a solvent of fats, oils, resins, caoutchouc, sulphur, phosphorus, iodine, alkaloids, etc. For the preparation of nitrobenzol, aniline and other derivatives.

TESTS. Pure benzol is a transparent liquid of spec. gr. 0.8846 at 15° C. It boils at 80.37° C. and solidifies at 0° to rhombic prisms. A higher boiling point indicates the presence of toluol and other homologues of higher boiling point and lower spec. gravity. It is insoluble in water, soluble in 4 parts of alcohol. Pure concentrated sulphuric acid dissolves pure benzol without coloration, forming benzol-sulphonic acid. Benzol should be free from more than traces of thiophene, C_4H_4S, which is present to the amount of ½% in crude benzol from coaltar. When a small amount of benzol containing thiophene is dropped on heated sodium, an alkaline sulphide is formed, as shown by the violet-blue color produced by sodium nitroprusside in a solution of the charred residue.

PREPARATION. The purest benzol is obtained by the dry distillation of 1 part benzoic acid with three parts of slightly moistened quicklime and rectification by fractional distillation. On the large scale, benzol is made for the manufacture of aniline by distillation of coaltar. The so-called *light oil*, which comes over between 60° and 150° C., is agitated with sulphuric acid to remove basic compounds; it is then washed with weak lye, and rectified by repeated fractional distillation. The final product is cooled with ice and the benzol crystals, which form at 0°, are separated and drained.

Benzo-purpurin, B, see *color reagents and indicators.*

BISMUTH COMPOUNDS.

BISMUTH HYDRATE, Bi O (O H).

USES. To convert, by heating in alkaline solution, metallic sulphides into their hydrates and oxides ; to convert arsenic trisulphide into arsenite, the pentasulphide into arsenate. In most cases the subnitrate may be substituted for it.

TESTS. It must dissolve in nitric acid without residue, and without becoming colored blue (copper). The absence of tin, antimony, arsenic and tellurium is shown by dissolving the hydrate in dilute nitric acid, precipitating with H_2 S and filtering. The precipitated bismuth sulphide is digested with ammonium sulphide, which should not extract anything soluble, so that when filtered and acidulated with H Cl only pure sulphur should be precipitated.

In the first filtrate from the precipitate by H_2 S in acid solution thallium may be recognized by neutralizing and adding potassium iodide, which would precipitate yellow thallous iodide. Iron and other metals of the fourth group would be shown by neutralizing with ammonia and adding ammonium sulphide. Silver, which is frequently present in bismuth compounds, is shown by precipitating the solution of bismuth hydrate in nitric acid with concentrated H Cl, when bismuth will remain in solution, while silver chloride precipitates and is blackened by sunlight. Copper may be shown either by ammonia or in small quantities by electrolytic deposition. For arsenic *Fleitmann's* test may be used (page 14).

PREPARATION. To insure bismuth hydrate (and other compounds) free from antimony, arsenic, tin, tellurium, silver, copper, thallium and iron, which, from being found in the bismuth ores, occasionally pass into the metal and the preparations made from it, it is best to start from a pure metal. Commercial bismuth is first purified by remelting at lowest heat in a shallow iron pan, slightly inclined. Arsenic is thus almost entirely volatilized, while most other impurities remain unmelted on the pan, the purer bismuth trickling off. It is again melted, and for every 1,000 parts a mixture of 45 parts of potassium cyanide and 17 parts of sulphur is stirred in, while the heat is increased. This converts the remaining arsenic, copper, etc., into sulphides, which separate from the melted bismuth. To free it from the last traces of impurities, the metal (or the commercial hydrate or subnitrate) is dissolved in nitric acid, avoiding excess. To the solution water is added until it

begins to get turbid, the liquid is left at rest to deposit the precipitate, from which it is decanted. Sodium (or potassium) hydrate is now added till the reaction becomes alkaline, and then concentrated glycerine, which redissolves the bismuth hydrate, but leaves other metals undissolved. To this solution there is then added a solution of 5 parts of glucose for one part of bismuth employed (freed from lime by addition of sodium carbonate) and the mixture left at rest in a well-closed flask, to reduce whatever silver and copper was present and deposit them as metallic silver and cuprous oxide. After filtration, bismuth is reduced by boiling and precipitates as a finely divided gray powder, absolutely pure from arsenic and other impurities. This is collected on a filter and washed.

From the pure metal the hydrate is prepared by dissolving it in nitric acid, precipitating by sodium hydrate, washing out and drying.

BISMUTH-POTASSIUM IODIDE, $Bi\,I_3 . 3K\,I$.

Dragendorff's Reagent.

USES. In the analysis of alkaloids this is used similarly to cadmium-potassium iodide. The addition of a few drops of its solution to 10 Cc. of an aqueous solution of alkaloids, acidulated with 2 Cc. of sulphuric acid, produces an amorphous orange precipitate with even very dilute solution of brucine, strychnine, curarine, atropine, physostigmine, aconitine, quinine, cinchonine, morphine, codeine, narcotine, papaverine, thebaine, delphinine, caffeine, berberine, bebeerine, nicotine and coniine. Narceine, theobromine, veratrine, digitaline and solanine are precipitated from concentrated solution, dilute solutions become only slightly turbid. Ammonia and alkaline hydrates and carbonates decompose the reagent to bismuth hydrate or carbonate. Urea, uric acid, hippuric acid, asparagin, creatine and creatinine are not precipitated. (*Dragendorff.*)

PREPARATION. Bismuth iodide is first prepared by subliming in a tube of hard Bohemian glass an intimate mixture of 4 parts of metallic bismuth (or 5 parts of bismuth sulphide) with 7 parts of iodine. The sublimate is dissolved in a warm, concentrated solution of potassium iodide, and as much more of this is added as was necessary for solution. The reagent is kept in the dark in well-closed bottles. It will not keep after dilution.

Fron's modification of Dragendorff's solution requires acidulating the alkaloid solution with strong H Cl, to prevent decomposition of the reagent. It is made by suspending 1.5 gr. of freshly precipitated bismuth subnitrate in 20 Cc. of water, heating to boiling and and adding 7 grammes of potassium iodide and 10 Cc. of H Cl.

BISMUTH-SODIUM HYPOSULPHITE.

(*Thiosulphate.*)

USES. To detect potassium whose salts are precipitated by the reagent as bismuth-potassium hyposulphite, of lemon-yellow color, entirely insoluble in alcohol. (*Campari.*)

PREPARATION. The reagent is only prepared when needed by dissolving bismuth subnitrate in as little H Cl as possible; sodium hyposulphite (thiosulphate) is at the same time dissolved in a minimum of water. Two or three drops of each solution are then mixed and added to 5 Cc. of strong alcohol. The colorless mixture produces the yellow precipitate in potassium salts.

BISMUTH SUBNITRATE, $Bi\ O\ N\ O_3 + H_2O$.

USES. For detection of glucose in urine, either by *Boettger's* method (adding the bismuth salt and sodium bicarbonate to the urine and heating), or by some of its modifications, in which an alkaline solution of bismuth is prepared from it. Among these, *Nylander's* solution appears to be most satisfactory. Also, in the same manner as bismuth hydrate, in converting arsenic sulphides into the corresponding oxides. Also for preparing other bismuth compounds.

TESTS. It should conform to the tests for absence of foreign substances enumerated under bismuth hydrate. Especially should freedom from arsenic be shown by *Fleitmann's* test (see Nitric Acid, page 14).

PREPARATION. Dissolve 1 part of pure, granulated bismuth in 6 parts of pure nitric acid of spec. grav. 1.25; apply heat enough toward the last (to finish the solution) to expel the red fumes and to reduce the volume to about one-third. Then pour into a large amount of pure water. Decant the acid liquid from the subsided precipitate, add more water and decant again several times, finally drain the precipitate and dry it at a gentle heat. If it should give off nitrous fumes it must be washed again.

Nylander's Solution is made by dissolving 2 gr. bismuth subnitrate and 4 gr. rochelle salt in a solution of 10 gr. sodium hydrate in 90 Cc. water, and separating the undissolved bismuth salt; one Cc. of this solution is added to 10 Cc. of urine or other saccharine liquid.

BISMUTH TETROXIDE, $2(Bi_2O_4) . H_2O$.

USES. For volumetric determination of manganese. It converts, in connection with nitric acid, the lower oxides of manganese into

permanganic acid, which may then be volumetrically determined by oxalic acid (*Leop. Schneider*).

PREPARATION. One part each of bismuth hydrate and potassium chlorate are intimately mixed and heated to redness. The mixture is then fused with two parts of sodium hydrate. The dark brown mass is washed out with water until it shows no more alkaline reaction, leaving a pale brown residue of sodium bismuthate, $Na\ Bi\ O_3$. This is triturated with dilute (5%) nitric acid, which dissolves out the sodium, evolves oxygen and leaves the red-brown hydrate of the tetroxide, which is washed and dried.

Black Flux, see *Fluxes*.

Bohlig's Reagent, see *Mercuric Oxychloride*.

Borax, see *Sodium Diborate*.

BRASS.

In the shape of foil, wire or turnings, brass is sometimes substituted for copper, zinc or gold to precipitate mercury from its salts; brass foil is used in *Hager's Kramato-method* for detection of arsenic.

BRAZILWOOD.

Pernambuco wood.

USES. To detect hydrofluoric acid and mineral acids in vinegar. The brazilwood and the closely allied sappanwood, both derived from varieties of cæesalpinia, contain a crystallizable yellow coloring principle, *Brazilin*, $C_{22}\ H_{20}\ O_7$, which, on exposure to light, changes to a reddish color. With sulphuric, nitric and hydrochloric acid it forms compounds of an intense peachbloom-red color. Hydrofluoric acid and many organic acids produce with it a bright yellow.

It is generally employed as a testpaper, made by immersing strips of unsized paper in a strong watery infusion of the wood. It must be prepared, dried and preserved with exclusion of daylight.

When a strip of moist brazilwood paper, slightly reddened by exposure to light, is exposed to the fumes of hydrofluoric acid it turns yellow. This serves especially in the blowpipe test of minerals containing fluorides, which are decomposed by microcosmic salt.

When brazilwood paper is immersed for half a minute in vinegar (or other liquids), containing even less than one-half per cent of sulphuric acid, and then dried, the color becomes a bright peachbloom-red. Hydrochloric or nitric acid produce a similar effect.

BROMINE, Br.

Atomic weight = 79.768.

USES. Bromine, being characterized by great affinity for hydrogen and for metals, serves, therefore, as an oxidizer, and for the conversion of metals into bromides, most of which are soluble in water. It sets free iodine from its compounds; it readily unites with sulphur, thus serving for the decomposition of sulphides; it liberates nitrogen from ammonia; it forms with phenol an insoluble tribromphenol, and thus is used for its detection and volumetric determination (*Koppeschaar*). In combination with alkalies (as hypobromite) it serves to decompose urea and to determine its quantity by measuring the resulting nitrogen (*Knop and Huefner*). In solution in water, hydrochloric acid or potassium bromide solution, it is useful for detection of alkaloids, being used instead of chlorine to produce the thalleioquine reaction with quinine and quinidine; also to precipitate cinchonidine, oxyacanthine, sanguinarine, hydrastine, bebeerine, etc. With bile colors it produces the characteristic color reactions. It is also used in the solid form, by impregnating cylinders formed of the silicious earth, called Kieselguhr (or, improperly, infusorial earth) in mineral assays, for the decomposition of natural metallic sulphides. (*A. Brand.*)

TESTS. At ordinary temperatures, pure bromine is a dark brown-red liquid, emitting orange-red vapors. At 15° C. its spec. grav. is 2.97; at —24.5° C. it becomes solid, and boils at 63° C. under normal pressure of 760 Mm. At 15° C. it dissolves in 33.3 parts of water, forming *bromine water*, which must be preserved in the dark, as in sunlight it is rapidly decomposed, forming oxygen and hydrobromic acid; potassium bromide, as well as hydrochloric acid, increases its solubility. It also dissolves in alcohol, ether, chloroform, etc., but gradually decomposes them, as well as cork, caoutchouc, etc.

Commercial bromine is seldom entirely free from chlorine and bromoform, but these may be disregarded in most operations, if not present in too large a quantity. To detect chlorine, the bromine is converted into barium bromide by neutralizing with pure baryta water, crystallizing the resultant mixture of barium bromate and bromide and heating the crystals to redness. The resulting barium bromide is entirely soluble in absolute alcohol, barium chloride being left as insoluble residue.

Absence of iodine may be shown by shaking an aqueous solution of bromine with ferric chloride and chloroform. Iodine would color the chloroform violet. When dissolved in solution of sodium hydrate no yellow drops should separate, nor any odor of bromoform be given off.

PREPARATION. Pure bromine may be made from the crude commercial article by repeated redistillation over powdered potassium bromide, rejecting the last portions of the distillate. The organic matter is entirely destroyed by passing the vapor over red hot manganese dioxide. It may be made absolutely pure by converting the bromine into barium bromide by high heat, dissolving in absolute alcohol and, after removal of the alcohol, distilling the pure salt with pure sulphuric acid and manganese dioxide.

Deci-normal solution of bromine is made by mixing 100 Cc. of deci-normal solution of potassium bromide, containing 11.8787 gr. $K\,Br$ in one litre, with 100 Cc. of deci-normal potassium bromate solution, containing 16.6667 gr. $K\,Br\,O_3$ in one litre, and with 10 Cc. of pure sulphuric acid. It contains 7.9768 gr. Br in one litre, but will rapidly decompose in the light. Paper dipped into a solution of starch and zinc iodide serves as indicator. It is employed for titration of phenol.

BROMOFORM, $C\,H\,Br_3$.

USED occasionally in petrographic work for mechanical separation of the ingredients of rocks by specific gravity. For this purpose the commercial article of spec. gr. 2.775 at 14.5 C. is of sufficient purity. It is often obtained as a bye-product of the bromine manufacture.

For other petrographic reagents see *Barium Mercuric Iodide*, *Cadmium Boro-tungstate* and *Mercuric Potassium Iodide.*

BRUCINE, $C_{23}\,H_{26}\,N_2\,O_4 + 2H_2\,O$.

USES. For the detection and approximate estimation of small quantities of nitric acid and nitrates, especially in drinking water. With nitric acid brucine produces an intense red color, rapidly changing to yellow (Kakoteline). It is used by adding to the water to be examined an equal bulk of a solution of 1 part of brucine in 300 parts of very dilute sulphuric acid. To this concentrated sulphuric acid is cautiously poured, so as to form a layer underneath. The red color appears at the zone of contact. Molec. Weight = 465.05.

TESTS. The commercial article is sufficiently pure. As it is obtained as a bye-product of the manufacture of strychnine, it may contain small amounts of other strychnos alkaloids, but they do not interfere with its use. It forms white, monoclinic crystals, soluble at 15° C. in 320 parts of water, 1.5 parts of alcohol and in 7 parts of chloroform.

CADMIUM COMPOUNDS.

CADMIUM BORO-TUNGSTATE, $2(Cd\,H_2\,W_2\,O_8).7(W\,O_3).B_2\,O_3 + 16\,H_2\,O$.

Klein's Reagent.

USES. For separations in petrographic work. A saturated aqueous solution of this salt has, at 15° C., spec. gr. 3.28. Crystals fuse at 75° C. in their water of crystallization, and this liquid has spec. gr. 3.6, and is sufficiently dense to float crystals of spinel.

PREPARATION. Six parts of sodium tungstate are dissolved in 30 parts of water and boiled with 9 parts of boracic acid. The solution is stirred while cooling and decanted from the crystals of borax, which separate. It is concentrated by evaporation and crystals removed as they form, until it becomes dense enough to float the glass stirring rod. Two parts of barium chloride, dissolved in a minimum of boiling water, are now added to the boiling solution. A dense white precipitate is formed, which is separated by filtration and washed with water. It is then dissolved in hot water containing 10% of concentrated hydrochloric acid. To the solution some more hydrochloric acid is added, and it is then evaporated to dryness. The dry mass is dissolved in boiling water, leaving an insoluble residue of tungstic acid. From the hot concentrated solution quadratic crystals of *barium borotungstate*, $2(Ba\,H_2\,W_2\,O_8).7(W\,O_3).B_2O_3 + 16H_2\,O$, form on cooling, and may be purified by recrystallization. To a boiling solution of the crystals a concentrated solution of cadmium sulphate is now added as long as barium sulphate precipitates. The liquid is filtered, and from it crystals of cadmium boro-tungstate are obtained by evaporation on a water bath. The salt is soluble in less than one-tenth of its weight of water.

It is used in a *Harada's separating funnel*, surrounded with a hot water jacket.

CADMIUM IODIDE, $Cd\,I_2$.

USES. To add to starch solution for the purpose of indicating the presence of chlorine, bromine, nitrous acid or other agents capable of liberating iodine from its compounds. It is preferred for this purpose to potassium or zinc iodide, on account of its greater stability and resistance to decomposition by light, etc., although it is not entirely unaffected by strong sunlight.

TESTS. The salt forms hexagonal plates of a white, pearly lustre, soluble in alcohol. At 20° C. one part requires 1.1 of water for solution. After protracted exposure to light $Cd\ I_2$ becomes yellow, and should then be rejected until purified again. Its aqueous solution, slightly acidulated with $H\ Cl$ and saturated with $H_2\ S$, should yield a pure yellow precipitate. The filtrate from this should, on evaporation, leave no permanent residue.

PREPARATION. Digest one part of pure metallic cadmium, in fine granules, with 2 parts of pure powdered iodine, suspended in 4 parts of water. After the solution has become colorless, filter it off from the small excess of cadmium, evaporate and set aside to crystallize.

Molec. weight = 364.884; Cd = 111.77; I = 126.557.

CADMIUM POTASSIUM IODIDE, $Cd\ I_2 . 2K\ I + 2H_2O$.

Marme''s Reagent.

USES. The solution of this salt produces in solutions of a great number of alkaloids, acidulated with $H_2\ S\ O_4$, flocculent precipitates, some of which soon become crystalline (nicotine, morphine, cinchonidine, etc.). They are easily soluble in alcohol and in an excess of the reagent; less so in water, insoluble in ether. From the precipitates the pure alkaloids are easily obtained by mixing them with solutions of alkaline hydrates or carbonates, and shaking out the free alkaloid with amyl alcohol, ether or benzol.

Strychnine and quinine are precipitated completely from solutions of 1 : 10000, and many other alkaloids (of opium, cinchona, strychnos, etc., etc.) in almost as great dilution; while the reagent fails to precipitate glucosides (such as salicin, amygdalin, digitalin, etc.), urea and ureides, caffeine, etc. (Marmè.)

PREPARATION. A concentrated solution of K I is divided into 2 equal parts. One of them is heated to boiling and cadmium iodide is added to it as long as it will dissolve. The other portion of K I solution is then added, and by concentration crystals of $Cd\ I_2 . 2K\ I + 2H_2\ O$ are obtained. A saturated solution may be preserved for a long time, while in dilution it rapidly decomposes

CALCIUM COMPOUNDS.

Calcium Carbonate, $Ca\ CO_3$.

USES. In assaying for iron or copper as a flux. The ordinary crystallized calcite is sufficiently pure.

CALCIUM CHLORIDE, $Ca\ Cl_2$.

USES. Anhydrous calcium chloride rapidly attracts moisture and deliquesces. It is therefore used to remove aqueous vapor from air or other gases. It is placed into cases of balances and desiccators so as to permit cooling, preservation and weighing of filters, precipitates, etc., dried by heat, without absorbing moisture again. In suitable tube apparatus it is used to absorb the water produced by the oxidation of hydrogen or otherwise liberated, and thus to determine its weight.

In solution $Ca\ Cl_2$ is used as a general reagent for separating organic acids into groups. One group (oxalic, tartaric, racemic, citric, malic, etc.) is precipitated, their neutral calcium salts being either insoluble or difficultly soluble in water, while those of other groups (succinic, benzoic, salicylic, etc., or acetic, formic, butyric, lactic, etc.) form soluble calcium salts.

Addition of a few drops of $Ca\ Cl_2$ solution to urine, in which glucose is determined by Fehling's solution, if made just before the finishing point, serves to promptly settle the cuprous oxide by entangling the suspended particles in the gelatinous calcium tartrate and thus facilitates the perception of the end of the reaction. (*Munk.*)

TESTS. For many purposes of drying the anhydrous $Ca\ Cl_2$ need not be pure. But for accurate gas analysis or for elementary organic analysis pure $Ca\ Cl_2$ is required. It should be white, dry and either in solid, fused fragments, or in pieces of spongy texture, offering a larger surface for absorption. When too highly heated during the process of fusion, the last portions of the hydrate will decompose into $Ca\ O$ and $H\ Cl$, leaving a product of alkaline reaction, capable of absorbing some $C\ O_2$.

The crystallized salt, $Ca\ Cl_2 + 6\ H_2\ O$, is used for making the solution, and must be strictly neutral. Its dilute solution must yield no precipitate with $H_2\ S$, nor with ammonium sulphide or hydrate, nor with calcium sulphate or barium chloride. After precipitation with a mixture of ammonium carbonate, hydrate and chloride, the filtrate must not be precipitated by sodium phosphate (absence of magnesium). No ammonia must be evolved on heating with calcium or potassium hydrate.

PREPARATION. Fragments of pure, white marble are added to dilute $H\ Cl$ (1:6) until no more is dissolved. Some lime water is added to the solution, and then $H_2\ S$ passed through it until a small filtered portion is no longer changed by ammonium sulphide. It is then poured into a flask, well corked and left for 24 hours in a warm

place to deposit sediment. The clear filtrate is then accurately neutralized with H Cl, evaporated and left to crystallize.

The crystals are dried on filter paper and either preserved to use for solution or made anhydrous by heating them until the opaque, dry mass, which at first results, fuses at the lowest possible temperature. The solution is prepared by dissolving 1 part of $Ca\,Cl_2 + 6\,H_2\,O$ in 5 parts of water.

CALCIUM FLUORIDE, $Ca\,F_2$.

Fluorspar.

USES. To prepare hydrofluoric and hydrofluosilicic acid. Also, with potassium or sodium acid sulphate in blowpipe analysis, to liberate alkalies (especially lithium) from their silicates and recognize them by their flame color. Pure ammonium fluoride or liquid hydrofluoric acid or powdered cryolite are often used in preference. It is best to select pure crystals of the mineral and powder them, rather than buy an often impure commercial powdered fluorspar.

CALCIUM HYDRATE $Ca\,(O\,H)_2$.

USES. Calcium hydrate (*slaked lime*) is used in the form of powder, in solution (as *limewater*), and in the intermediate state of a thin magma (as *milk of lime*). Lime water serves to detect carbon dioxide by the formation of insoluble calcium carbonate; also to recognize tartaric and citric acids, etc. In the form of milk or dry powder it is used to liberate ammonia from its compounds and to separate magnesia from the alkalies by converting magnesium salts in the insoluble hydrate, requiring 55,000 parts of water for solution. It is also used in the separation of alkaloids from the crude drugs; in the making of calcium hypochlorite and other preparations, among them the *soda-lime*, employed in ultimate organic analysis for determining the nitrogen in the form of ammonia.

TESTS. For some purposes the ordinary burnt lime furnishes preparations of sufficient purity, but for others a strictly pure article, free from alkalies, barium, strontium or magnesium, must be used. Alkalies are most easily detected by the spectroscope, the hydrate being for this purpose converted into chloride by adding H Cl. Limewater is quickly changed by the $C\,O_2$ of the atmosphere, and must, therefore, from time to time, be tested for strength, by giving a strong alkaline reaction with test papers, and precipitate with sodium carbonate; or else kept saturated by keeping it in contact with excess of solid hydrate. At 15° C., one part of calcium hydrate requires 780 parts of water for solution. It should give no

precipitate with solutions of calcium sulphate, potassium chromate or barium chloride. After precipitation with a mixture of ammonium carbonate, chloride and hydrate, the filtrate on evaporation should leave no permanent residue.

PREPARATION. When only absence of alkalies is required, the ordinary hydrate may be freed from them by repeated boiling in a silver dish with distilled water, before making the solution or milk, or drying again for use in powdered form. Absolutely pure hydrate is made from pure calcium chloride by precipitating its solution with excess of ammonium carbonate, washing and drying the precipitate and then calcining it in a platinum crucible by protracted application of a bright red heat until a small specimen no longer shows effervescence with dilute nitric acid.

It is slaked by addition of one-half its weight of pure water and, after cooling, the product is preserved in close vessels.

CALCIUM HYPOCHLORITE, $Ca\,Cl_2 \,.\, Ca\,(O\,Cl)_2$.

Chlorinated Lime. Bleaching Powder.

USES. For a number of purposes for which chlorine is employed. For making solutions of alkaline hypochlorites; converting alcohol, acetone, etc., into chloroform. For recognizing aniline by the violet-blue color produced with hypochlorite alone, turned into rose-red by addition of ammonium sulphide; for liberating nitrogen from urea; for distinguishing the spots of antimony from those of arsenic produced in Marsh's test, As being soluble, Sb insoluble. For the convenient evolution of chlorine gas, bleaching powder is made into small cubes with plaster of paris, which are acted on by H Cl in an apparatus similar to that for evolving $H_2\,S$.

TESTS. A good commercial article is of sufficient purity, provided it is free from arsenic. Its strength in available chlorine should not be less than 25%, the highest possible limit being 52.17. This is ascertained by titration with deci-normal sodium arsenite solution, of which 1 Cc. = 0.003537 Cl.

Of the hypochlorite, 7.074 grammes are thoroughly mixed by trituration with water sufficient to fill a 1 litre flask. After subsidence, 50 Cc. of the clear liquid (corresponding to 0.3537 gr. of hypochlorite) are transferred to a flask and deci-normal solution of sodium arsenite added from a burette until a drop taken out fails to give a blue color on starch paper prepared with zinc iodide. Each Cc. of arsenite used indicates one per cent of available chlorine.

PREPARATION. On the large scale chlorinated lime is manufactured by passing chlorine gas into chambers containing, on shallow

shelves, freshly slaked lime, keeping the temperature below 25° C., so as to prevent the formation of chlorate.

CALCIUM SULPHATE, $Ca\,S\,O_4 + 2H_2O$.

Gypsum, Plaster of Paris.

USES. In saturated aqueous solution calcium sulphate is used to detect barium, strontium and oxalic acid. Moulded into small cylinders it is introduced into tubes to furnish water, as it relinquishes its water of crystallization by heating. The partially dehydrated plaster of paris is used as a cement, etc. Also in blowpipe analysis and assaying to fuse with fluorspar, etc. Molec. W. = 171.784.

TESTS. Pure natural crystals of transparent gypsum (selenite) are selected. They require for solution at 15° C. 380 parts of water.

PREPARATION. Into the bottles filled with pure water small fragments of crystals are introduced, so as to remain in excess and insure full saturation.

CARAMEL.

USES. A solution of caramel containing 100 grammes in 1 litre is used in sugar refineries as a standard of comparison for ascertaining the decolorizing power of boneblack.

PREPARATION. Sugar is carefully heated to between 180° C. and 200° C., and thus converted into dark-brown caramel. Of this 100 gr. are dissolved in 200 Cc. of water, and 100 Cc. of alcohol added, then diluted to 1 litre. After standing for some days, to allow depositing the sediment, the liquid is filtered and preserved.

CARBON DISULPHIDE, $C\,S_2$.

USES. As a general solvent of oils, fats, resins, gutta percha, caoutchouc, etc.; also of phosphorus, sulphur, iodine, arsenic chloride, bromide or iodide, etc. As a special reagent for the recognition of iodine, which dissolves in it with a beautiful violet color; for alcohol by the formation of cuprous ethyl-xanthate. For the preparation of potassium sulphocarbonate, $K_2\,C\,S_3$, used for the detection of nickel, etc.

It is also used to identify cod liver oil. One drop of the oil added to 20 drops of carbon disulphide and 1 drop of conc. sulphuric acid produce a beautiful violet color, which soon fades.

TESTS. Pure carbon disulphide is a mobile, colorless, very volatile and highly refractive liquid of peculiar odor, rather agreeable

when pure, but very fetid when impure, especially when containing selenium or organic sulphides or mercaptans. At 15° C. its sp. gr. is 1.268; it boils at 46° C., but volatilizes at a much lower temperature. In water it is almost insoluble, but mixes in all proportions with alcohol and ether.

The substances most frequently found as impurities are sulphur, sulphur dioxide, hydrogen sulphide and sometimes selenium and other impurities. Moist test papers should show neutral reaction (abs. of $S\,O_2$); lead carbonate or lead acetate solution should not be colored black or brown (abs. of $H_2\,S$); on spontaneous evaporation, on a watch glass, no residue should remain (abs. of more than traces of water, sulphur, arsenic compounds, etc.) The odor should not be fetid nor the color yellow.

PREPARATION. The use of absolutely pure carbon disulphide by perfumers for extracting the odors of flowers has caused it to be manufactured largely at very low prices, so that few will incur the risk of preparing or rectifying $C\,S_2$ on a small scale. It is made by heating in a suitable distilling apparatus of stoneware or iron (Schroetter's) pieces of pure charcoal to a bright red heat, and then introducing, through a side tube, pieces of pure sulphur. The vapor is condensed and rectified by redistillation at a temperature not exceeding 50° C.; the distillate is shaken with solution of potassium permanganate, decanted and, if necessary, redistilled at a low temperature.

CERIUM DIOXIDE, $Ce\,O_2$, and CERIC HYDRATE, $Ce_2\,O\,(O\,H)_6$.

USES. This has been recommended by *Sonnenschein*, under the older name of ceroso-ceric oxide, as one of the most delicate reagents for strychnine. When a small amount is brought together with strychnine and concentrated sulphuric acid the same series of colors are produced as with other oxidizers, potassium dichromate, permanganate, lead dioxide, manganese dioxide, etc. A deep blue at first, passes through violet into red. The cerium produces the reaction with smaller amounts of strychnine and the successive colors change much more slowly, so as to give better opportunity for observation. The hydrate being more soluble is preferable to the anhydrous dioxide.

TESTS. Cerium salts are rarely found in commerce entirely free from didymium and lanthanum, but these do not interfere unless in too great a quantity, so it is best to test the specimen to be used by producing the colors with a minute crystal of strychnine and sulphuric acid,

PREPARATION. The anhydrous oxide is obtained by heating to redness either the oxalate or the nitrate of cerium. The hydrate is formed by precipitating cerous hydrate from a solution of the nitrate or oxalate by the addition of potassium hydrate. This is kept stirred up in the solution while either chlorine gas is passed through (or solution of calcium hypochlorite is added), until the precipitate has been converted into the brownish-yellow ceric hydrate, $Ce_2O(OH)_6$. This is separated by filtration, washed, dried and carefully preserved.

CHARCOAL.

USES. In solid pieces, wood charcoal serves as a support in blow-pipe operations; also for purifying alcohol from fusel oil previous to rectification by distilling. In powder, different varieties of carbonaceous material, wood, charcoal, coke, lampblack, etc., are used for the reduction of oxides, etc., at high temperature. (Preparation of potassium iodide, bromide, barium sulphide, etc.) Animal charcoal, principally boneblack, is used for the removal of coloring materials in the purification of alkaloids, sugar, urine, etc.

For blow-pipe supports, a thoroughly burned charcoal, derived from pine or other soft wood, is preferable. It should be selected of straight, parallel fibre, free from knots or bark, and split into pieces of five to six inches in length, two inches broad and about three-quarters to one inch thick, the surface used presenting a radial section. Finely powdered charcoal, compressed into pieces of suitable shape and size, are now sold for the same purpose.

CHINOIDINE IODOSULPHATE.

USES. This reagent has been introduced by *De Vrij* for the estimation of quinine in a mixture of cinchona alkaloids, by precipitation as herapathite. Its use is based on the difference in solubility of the iodosulphates (herapathites) of the cinchona alkaloids. The assay is made as follows: In a beaker, very gently heated on a water-bath, 1 gramme of the alkaloids is dissolved in a mixture of 19.69 grammes alcohol of 94% and 0.31 gr. sulphuric acid, and, after solution, 30 grammes alcohol are added. The solution of the reagent is then added, drop by drop, with constant stirring, until the color of the solution has become an intense yellow. This is due to the yellow cinchonidine iodosulphate remaining in solution, while the darker quinine salt precipitates, showing red stripes whenever the beaker is rubbed by the stirring rod. The heat is now increased sufficiently to redissolve the precipitated quinine salt, and the beaker is set aside for twelve hours to deposit the crystals, which are weighed. One part of herapathite corresponds to 0.55055 of quinine.

PREPARATION. On a water bath dissolve 2 parts of chinoidine in 4 parts of benzol; after cooling, decant the clear liquid and agitate it thoroughly with 2 parts of dilute sulphuric acid (1 : 10). Transfer to a porcelain capsule, and add to it a solution of one part iodine and two parts potassium iodide in 50 parts of water, drop by drop, and with constant stirring. Chinoidine iodosulphate precipitates. After washing it by repeated addition of water and decanting, one part is dissolved in six parts of alcohol, by careful heating on a water bath. The solution is set aside to cool and deposit its less soluble portion. The clear liquid is separated, evaporated almost to dryness, and one part of the residue is dissolved in five parts of cold alcohol and carefully preserved.

CHLORAL HYDRATE, $C_2Cl_3HO + H_2O$,

USES. When chloral hydrate is brought together with an alkaline sulphide, especially ammonium sulphide, a deep red-brown precipitate is formed, of such intensity of color that the reaction may be used, not only for the recognition of chloral, but also for ammonia, and for H_2S. Chloral hydrate dissolved in freshly saturated sulphuretted hydrogen water produces, with even small traces of ammonia, a distinct yellow to red-brown; when dissolved in ammonia water it serves, by the same reaction, to detect small amounts of hydrogen sulphide.

Chloral hydrate also serves to detect naphthol. The substance containing the naphthol is dissolved in concentrated solution of potassium hydrate. On addition of a small crystal of chloral hydrate (or a drop of chloroform), and heating, it turns deep blue, if even traces of naphthol are present (*Lustgarten*).

Chloral hydrate, as well as the alcoholate and metachloral, have also been proposed as aids in differentiating essential oils, for recognition of digitalin, etc.

A solution of 12% of chloral hydrate is used in microscopical investigations to render transparent some vegetable tissues, e. g., the epidermis of wheat or rye grains, etc. It is also used to dissolve alkaloids, and for this purpose a solution in 4 parts of glycerin is sometimes employed instead of the above, in water. Also for preparing trichloracetic acid.

TESTS. For all the above purposes crystals of chloral hydrate, as now sold, are sufficiently pure.

PREPARATION. By passing dry chlorine gas slowly, but without intermission for several weeks, into alcohol of no less strength than

0.8086 spec. grav. (97% by volume, or 95.34% by weight). When no more hydrochloric acid gas is formed, even by raising the temperature to 65° C., the product is heated with an equal volume of conc. sulphuric acid, distilled, purified by redistillation and then converted into hydrate by addition of the necessary amount of water. Chloral, $C_2\,Cl_3\,H\,O$, = 146.018; chloral hydrate, $C_2\,Cl_3\,H\,O + H_2\,O$ = 163.978.

CHLORINE Cl and CHLORINE WATER.

USES. To convert metals and their oxides into chlorides, thereby rendering them soluble, e. g., gold, platinum, etc.; to decompose sulphides; to liberate bromine and iodine from their compounds. To oxidize in the presence of water a number of bodies, by uniting with the hydrogen to form hydrochloric acid, while oxygen is liberated. It is hence employed in the oxidation of nickel, in the preparation of ceric hydrate, ferricyanides; in the quantitative determination of bromine and iodine in their silver salts, etc. In organic bodies it is capable of substituting H, e. g., in the preparation of chloral, in bleaching indigo, etc. It also serves as a special reagent for quinine and quinidine (thalleioquine reaction). It is used either as gas, well dried, or in saturated watery solution as chlorine water.

TESTS. Chlorine water must be well saturated, and, as it rapidly deteriorates, even by the most careful keeping, should be frequently renewed. It may be examined with volumetric arsenic solution, as described under calcium hypochlorite, q. v. It should not contain hydrochloric acid (as it will when long or carelessly kept). This may be ascertained by shaking with some metallic mercury until the odor has entirely disappeared, when the acid reaction of the liquid will indicate the presence of H Cl. When shaken with chloroform or carbon disulphide, these reagents must not become colored, even transiently; a brownish color would indicate bromine; a violet, iodine.

Dry chlorine gas has a greenish-yellow color; specific grav. 35.37 (H = 1). It is very corrosive, irrespirable, and shows great affinity for hydrogen. It is tested by dissolving in water and examining as above.

PREPARATION. Chlorine may be prepared in a variety of ways; by bringing together hydrochloric acid with potassium permanganate or dichromate, or manganese or lead dioxide, etc. The best method is that of Wiggers: A capacious flask is fitted with a safety-funnel tube and a delivery tube. The latter communicates with a small wash bottle containing water (or in case dry gas is to be used, concentrated sulphuric acid). From this, a tube leads

to a U tube containing fragments of $Mn\ O_2$, to remove $H\ Cl$, and then connects with the apparatus for decomposition, or with the flask containing water to be saturated. Into the evolution flask is placed an intimate mixture of 15 parts of high grade manganese dioxide (free from lower oxides of manganese and from limestone), with 18 parts of dry sodium chloride. To this a cooled mixture of 45 parts of conc. sulphuric acid (free from arsenic) and 21 parts of water is added, and the mixture thoroughly shaken together. The flask is now closely attached to the apparatus and, after rejecting the first portion, contaminated with the air in the apparatus (and containing bromine, if any was present in the salt), the chlorine is used to saturate the water or for other purposes.

After saturation, the chlorine water must be preserved in well-closed bottles, in a cool place, with perfect exclusion of light. Ample precautions must be taken to avoid inhalation of the gas.

Recently, *Winkler* has proposed to prepare chlorine from hydrochloric acid and calcium hypochlorite, the latter being made up into cubes of suitable size by admixture with plaster of paris. A Kipp's apparatus is employed, and renders the regulation of the supply of chlorine easy.

CHLOROFORM, $C\ H\ Cl_3$.

USES. Chloroform is employed as a solvent for iodine, bromine, phosphorus, sulphur, etc.; for gutta percha, caoutchouc, Canada balsam, resins, oils, fats, paraffin, many alkaloids, etc. Hence, it is useful for removing these substances from mixtures, for recognizing iodine by the violet color of the solution; for differentiating alkaloids according to *Dragendorff's* process by successive application of various solvents (benzin, benzol, chloroform, amyl alcohol, etc.). Also, for the assay of cinchona barks a mixture is used by *Prollius* consisting of 20 parts of chloroform, 76 parts alcohol and 4 parts of ammonia water, the chloroform being substituted in special cases instead of the ether usually employed. It also forms a very delicate reagent for the detection of naphthol by the production of a blue color by boiling it for some minutes with its alkaline solution (*Lustgarten*). To detect even minute quantities of aniline (*Hoffmann*) and aniline dyes, rosaniline derivatives, etc. (*Curtman*), by the production of malodorous isonitrils, when heated with them and alcoholic solution of alkaline hydrates. In wine analysis it serves to detect adulterations with various coloring materials (cochineal, elderberries, red currants, logwood, rose or poppy petals, etc.) (*De Groot*). Mol. W. = 119.084.

TESTS. Pure chloroform is a colorless, volatile liquid of a burning, sweetish taste and a peculiar ethereal odor. Spec. grav. at 15°

C., 1.499. It is readily decomposed by light and air; hence, it should be preserved as much as possible excluded from both. Addition of a small amount of pure alcohol protects it from change and is not objectionable for analytical purposes. Choroform boils at 60°—61° C. It is soluble at 15° C. in 200 parts of water, and mixes with alcohol in all proportions. When purified with impure oil of vitriol it is liable to contain arsenic, and must, therefore, be tested for its absence. Its solution in water must be neutral to test papers; it must give no precipitate with silver nitrate (abs. of free chlorine and arsenic). At ordinary temperatures it must completely volatilize without residue. In contact with pure conc. H_2SO_4 no brown color must appear. It must not liberate iodine from a solution of pure potassium iodide; hence, no violet color must be produced by mixing them.

PREPARATION. On the large scale, chloroform is made by distilling 320 parts of bleaching powder (35% of active chlorine) with 100 parts of strong alcohol, U. S. P. The distillate is rectified after agitation with conc. sulphuric acid. By using acetone instead of alcohol a purer product is obtained in greater abundance.

On a small scale, pure chloroform may be prepared by distilling 3 parts of chloral hydrate with a solution of 1 part of potassium hydrate in 10 parts of water, and purifying the product by redistillation from a water bath.

CHROMIUM COMPOUNDS.

Chromic Acid, see page 6.

CHROMIC ALUM, $Cr_2K_2(SO_4)_4 + 24\ H_2O$, and CHROMIC SULPHATE, $C_2(SO_4)_3 + 18\ H_2O$.

USES. A few drops of the watery solution of either of these salts are added, together with some ammonium chloride, to volumetric solution of gelatine for titration of tannic acid for the purpose of facilitating the separation of the flocculent precipitate, and thus determining the final point (*Johanson*).

The commercial articles are of sufficient purity.

CHROMOUS CHLORIDE, $CrCl_2$.

USED as an absorbent of oxygen in gas analysis (*Von der Pfordten.*)

PREPARATION. Two parts of chromic acid are heated with 15 parts of hydrochloric acid of spec. gr. 1.16, and the resulting green solution of chromic chloride is reduced to blue chromous chloride

by immersion of metallic zinc. This is done within the gas absorption apparatus, so as to use the solution before coming in contact with air. By absorption of oxygen the blue solution turns green.

CINCHONAMINE, $C_{19} H_{24} N_2 O_2$.

USES. This alkaloid occurs in a dark brown variety of cinchona bark from Colombia; its nitrate, $C_{19} H_{24} N_2 O_2 . H N O_3$, is almost insoluble in water, acidulated with nitric or acetic acid, and upon this insolubility the method of *Arnaud and Pade* for determining nitric acid in nitrates by precipitation is founded. The alkaloid is by careful neutralization with sulphuric acid converted into sulphate $(C_{19} H_{24} N_2 O_2)_2 . H_2 S O_4$, which is easily soluble in water, and with this solution the soluble nitrates are precipitated. The molecular weight of $C_{19} H_{24} N_2 O_2$ is 311.39.

TESTS. The alkaloid crystallizes is colorless, anhydrous prisms; melts at 195° C. and turns polarized light to the right $[(\alpha)_D = + 117.9]$. It is insoluble in water; at 17° C. it dissolves in 100 parts of ether and in 31.6 parts of 90% alcohol. The taste is only feebly bitter; the solution of the sulphate does *not* fluoresce.

Citraconic Acid, $C_5 H_6 O_4$.

This acid, obtained by distilling dry citric acid, is occasionally used for the separation of primary from secondary and tertiary amines. The primary amines form with it amides (resp. anilides), which, on account of less volatility, are, on distillation, retained as residues, while the secondary and tertiary distil over (*Michael*).

COBALT COMPOUNDS.

COBALTOUS NITRATE, $Co (N O_3)_2 + 6 H_2 O$.

USES. Cobaltous nitrate is used in blowpipe analysis, especially for the detection of aluminium salts, which give with it an opaque, blue mass (Thenard's blue), and of zinc salts which, on heating with it, give a yellowish green (Rinmann's green). These reactions, however, furnish no absolute proof of the presence of aluminium and zinc, for cobaltous nitrate produces a transparent blue glass with alkaline phosphates, borates and silicates and an opaque blue, not only with aluminium, but also with earthy phosphates and silicates; and a green of various shades with tin, titanium, antimony and niobium compounds. Those of magnesia and tantalic acid produce a flesh-colored mass; barium, a brown-red; beryllium, calcium and strontium, a gray mass.

TESTS. The impurities most likely to occur in cobalt compounds arise from the metals ordinarily associated with it in the ores: nickel, iron, manganese, copper, silver, bismuth, arsenic, lime, magnesia, etc. Its solution, acidulated with H Cl, should give no precipitate with hydrogen sulphide. After precipitating the aqueous solution with ammonium sulphide, the filtrate should, on heating upon platinum foil, leave no fixed residue. When to the solution potassium cyanide is added until the precipitate is redissolved, and then bromine or sodium hypobromite added, no black precipitate of nickelic hydrate should fall, even after an hour's time. The cobaltous nitrate of commerce is generally of sufficient purity. $Co\,(N\,O_3)_2 + 6\,H_2\,O = 270.449$.

PREPARATION. The pure metal is dissolved in dilute nitric acid, the solution concentrated and crystallized. A 10% solution in water is usually employed.

Pure metallic cobalt may be obtained by the following process: Any rich cobalt ore, either the speiss cobalt (smaltine), $Co\,As_2$, or cobalt glance (cobaltine), $Co\,As_2 \,.\, Co\,S_2$, or earthy cobalt, is finely powdered and roasted until all volatile ingredients are driven off. Ten parts are then mixed with one part of ferrous sulphate, and the mixture is introduced, in small portions, into a hessian crucible containing 30 parts of potassium disulphate fully melted.

The heat is continued until the mixture is thoroughly fused and all evolution of sulphuric acid vapor has ceased. It is then extracted by boiling water, which extracts cobaltous sulphate, leaving behind the arsenic as ferric arsenate, and most of the iron and nickel, calcium sulphate, etc. The filtered solution is slightly acidulated and saturated with hydrogen sulphide, so as to precipitate the metals of the fifth and sixth analytical groups. It is again filtered, hydrogen sulphide expelled by boiling, and a concentrated solution of potassium nitrite, and then acetic acid is added. After complete precipitation, the yellow potassium-cobaltic nitrite, $Co_2\,(N\,O_2)_6 \,.\, 6\,K\,N\,O_2$ (Fischer's salt) is separated by filtration and thoroughly washed with cold water. It is then dissolved in boiling hydrochloric acid; the solution, containing cobaltous chloride and potassium chloride, is concentrated by evaporation and mixed with about an equal volume of ammonia water and ten per cent solution of ammonium chloride, and set aside for several days, covered so as to admit free access of air. When the color has become a pure red purple, and when a small sample no longer turns blue on adding an excess of hydrochloric acid, it is supersaturated with hydrochloric acid, and the temperature raised to boiling heat. Nearly the entire amount of cobalt separates in crimson-colored, quadratic crystals of *purpureo-cobalt chloride*, $Co_2\,(N\,H_3)_{10}\,Cl_6$. This is heated

to redness in a current of hydrogen, when pure metallic cobalt remains as a gray powder.

LUTEO-COBALTIC CHLORIDE, $Co_2(NH_3)_{12}Cl_6$.

USES. This reagent produces at once in a solution of alkaline pyrophosphates a crystalline orange-colored precipitate, which does not form with ortho or metaphosphates until the lapse of considerable time. Hence, it serves to distinguish and separate pyrophosphoric acid (*Braun*).

PREPARATION. Cobaltous chloride is first made by dissolving 6 gr. of metallic cobalt in 22 Cc. of conc. hydrochloric acid and obtaining crystals by concentration. A mixture of 1 part of cobaltous chloride, 1 part ammonium chloride, 1 part potassium permanganate and 6 parts of concentrated ammonia water is then heated in a closed vessel for 24 hours to 70° C. The orange-colored liquid is separated by filtration, and any crystals remaining in the residue are redissolved out by boiling water containing 5 per cent of hydrochloric acid. The solution is evaporated somewhat, and then an excess of very cone. hydrochloric acid is added. This precipitates the luteo-cobaltic chloride in brownish-yellow crystals, which may be purified by recrystallization from boiling water. The test solution is made by dissolving one part of the reagent in 20 parts of water.

SODIO-COBALTIC NITRITE, $Co_2(NO_2)_6 . 6 NaNO_2$.

USES. For the detection of potassium, with which it forms a yellow precipitate, $Co_2(NO_2)_6 . 6 KNO_2 + \times H_2O$ (*Fischer's salt*), which is hardly soluble in cold, somewhat more in hot water, insoluble in alkaline chlorides, nitrites, acetates or in dilute acetic acid. It dissolves in boiling hydrochloric acid. Cæsium, rubidium and ammonium salts form similar precipitates. Potassium salts are precipitated from very dilute solutions, where platinic chloride no longer shows a reaction. As no precipitate is formed with the salts of the alkaline earths, zinc, magnesium or iron, they need not be removed from solution before application of the reagent for the precipitation of potassium (*Curtman*).

PREPARATION. A solution of 4 grammes cobaltous nitrate is mixed with one of 10 gr. sodium nitrite, both in very little water, and 2 Cc. acetic acid are added and then water to fill up to 100 Cc. (*Curtman*). Cobaltous chloride may be used instead of nitrate (*L. L. de Koninck*).

Cobalt paper is occasionally used as an indicator for "spotting," in the volumetric determination of zinc, copper, etc., by sodium sulphide. It is made by dipping strips of filter paper into an alco-

holic solution of cobaltous chloride, colored by a little aniline blue, so that only one-half of the length of the strip becomes stained, while the other half remains white. A drop of the mixture to be tested for excess of sulphide is placed on the white end, so that by spreading over the paper the liquid may reach the stained end and color it black in case of an excess of the sulphide.

Cochineal; see *Color Reagents and Indicators,* page 77.

COLOR REAGENTS AND INDICATORS.

Under this designation a number of various coloring agents are described, which have the property of forming with acids and with alkalies compounds different in color, so that in neutralizing acids or alkalies, and especially in *volumetric analysis*, they indicate the point of neutralization. Others serve as *colorimetric reagents* by observation of the various degrees of intensity of color, produced by different amounts of the colored compounds, produced by them with certain chemicals. Some of them are derived directly from plants or animals, others are artificial products prepared from aniline, phenol, anthracene, naphthalin and other aromatic compounds produced by the coaltar industry. Nearly all of them are used only in small quantity and the state in which they are found in commerce, as manufactured on the large scale for the purposes of the dyer and calico printer; hence, in most cases, there is no occasion to describe tests for their purity, nor processes for preparing them on the small scale. Many of the indicators will serve equally well for all general purposes, but there are distinct features in the behavior of several of them, which make them valuable for differentiation. Thus, litmus and phenol-phthalein indicate alkaline reaction with hydrates and carbonates, but not with dicarbonates, while methyl-orange, lacmoid, Poirier's blue, etc., show the alkaline reaction with dicarbonates as well. Phenol-phthalein does not show the alkaline reaction with aniline, toluidine or quinoline, but reacts with the acids of their salts as if no base was present; litmus remains unaffected by them, while methyl-orange shows the alkaline reaction of the free bases. Urine, which shows acid reaction with litmus and phenol-phthalein, gives an alkaline reaction with lacmoid on account of the bases of the phosphates, etc., etc.

Thus, by a judicious use of different indicators, valuable information may be obtained.

Aurin; see *Rosolic Acid*, page 19.

BENZOPURPURIN B., $C_{34}H_{28}N_6O_6S_2Na_2$. This is one of the tetrazo-tolidine colors, allied to congo-red. Its aqueous solution is *orange-red*, turning *violet* on addition of acids; *red* with alkalies. While useful for general purposes it is especially so in the titration of pyridine, which does not give an alkaline reaction with litmus or tropæolin, while ethyl-orange and benzopurpurin B. show with it alkaline reaction. Paper saturated with its solution, rendered violet by a minimum of acid, forms a very delicate reagent for traces of gaseous ammonia.

Brazilwood, see on page 58.

CABBAGE, RED. The leaves to water or dilute alcohol yield a *violet* color; turned *red* by acids; *green* by alkalies. It is suitable to all purposes of alkalimetry, including ammonia. Paper stained with it makes a very sensitive test paper.

Cobalt paper; see *Cobalt Compounds*, page 75.

COCHINEAL. The insect contains a coloring material, soluble in water and alcohol, whose principal constituent is *carminic acid*, $C_{17}H_{18}O_{10}$. The tincture is made by macerating 1 part of the whole cochineal with 80 parts of 20 to 25 per cent alcohol. It reddens litmus paper. The color is a *yellowish-red*, turned *violet* by alkalies, restored by acids and shows well by artificial light. Salts of iron, alumina, lead, copper and alkaline acetates interfere. The tincture is very sensitive to alkalies and alkaline earths, even their carbonates and dicarbonates producing the violet color; hence, it is for these preferable to litmus, and stands equal to lacmoid; for ammonia it is superior to phenol-phthalein; for organic acids, it is less sensitive and inferior to litmus. By soluble lead salts, even in very dilute solution, it is colored a peculiar purple-violet and is, therefore, used to detect lead in drinking water. It is also employed for staining vegetable tissues in microscopic investigations.

COLEUS VERSCHAFFELTI. The strong alcoholic tincture of the deep red leaves of this common garden plant has been recommended by *Boettger*; it turns *green* with alkalies, *red* with acids. It contains the purple, resinous Colein, $C_{10}H_{10}O_5$.

CONGO RED, $C_{32}H_{22}N_6O_6S_2Na_2$, a naphthyl-amine-tetrazo-benzidine color, made by the action of tetrazo-diphenyl chloride on naphthionic acid. It dissolves in water with a bright red color, changed to *blue* by acids and restored to *red* by alkalies. It indicates free mineral acids by a blue color, even if only a trace is

present (0.0019% of H Cl), while neither acid salts, such as aluminium sulphate, potassium dichromate, etc., nor acetic or other organic acids produce any change. On the other hand, it is very sensitive to a number of alkaloids, to aniline, toluidine, etc., which restore to red the color changed to blue by acids, so that it proves a useful indicator for their titration. It is extensively employed in the clinical analysis of gastric juice, in which it indicates the smallest traces of free hydrochloric acid. It is useful in testing acetic acid, which, when pure, does not change its red color, while the presence of a trace of sulphuric or hydrochloric acid turns it blue. It is generally used as *congo paper*, made by soaking unsized paper in a watery solution of 1%, and drying. The color is retained firmly, even if the paper is thrown into liquids.

Corallin: a compound of aurin and methylaurin; see *Rosolic Acid*, page 19.

CURCUMIN W. The commercial name for a stilbene color, soluble in water with *greenish-yellow* color, and turning *red* with the least trace of alkali. Like phenol-phthalein, it does not indicate dicarbonates. It is suitable for titration of ammonia.

CYANIN or QUINOLINE-BLUE, $C_{29} H_{35} N_2 I$, used for sensitizing photographic dry plates; crystals of green metallic lustre, soluble in alcohol; is occasionally used as indicator. It turns *blue* with alkalies, *colorless* with acids.

m DIAMIDO-BENZOL or *m* PHENYLENE-DIAMINE, $C_6 H_4 (N H_2)_2$ (1 : 3), is obtained, in the form of a grayish crystalline powder, by the reduction of meta-dinitrobenzol. It is a strong base, little soluble in water, easily dissolved by alcohol or ether. It serves for the detection of nitrites, especially small quantities found in drinking water. The free nitrous acid (liberated from the nitrites by sulphuric acid) produces with it a yellow color, so intense that even traces of it become visible. Hence, phenylene-diamine may be used as a colorimetric indicator, and by comparison of color with a standard of known strength an approximate quantitative determination may be made. For water analysis one part of meta-phenylene-diamine is dissolved in 200 parts of water. Of this solution, 1 Cc. is added to a mixture of 100 Cc. of the water under examination with 1 Cc. of dilute sulphuric acid (1 : 3).

DIMETHYL-AMIDO-AZOBENZOL-SUPHONIC ACID, $(C H_3)_2 N . C_6 H_4 . N : N . C_6 H_4 . S O_3 H$, is known in commerce as *Helianthin* (see page 21), *Methyl Orange*, Poirier's *Orange*, *III*, or *Tropaeolin*, *D*. This, as well as its base, is a useful indicator; the base being by some preferred on account of a greater difference in the (+) *yellow* color of

alkalies and the (—) *crimson red* of acids. But they are nearly of equal value, and the sulphonic acid is more easily procured. The description of their application will answer for both.

The yellow solution is turned crimson red by even small traces of free mineral acids and restored by alkalies. Neither hydrogen sulphide, arsenous nor carbonic acid interfere with this effect. It is suitable as indicator for hydrates, carbonates, dicarbonates, borates, silicates, arsenites and sulphides of the alkalies and alkaline earths; also for all free mineral acids, especially for the titration of phosphoric acid, in which the change from (—) red to (+) yellow occurs as soon as the primary salt, $Na\,H_2\,P\,O_4$, is formed. It will show alkaline color with aniline, toluidine, quinoline and many alkaloids, which do not show any reaction with phenol-phthalein. It cannot be used in hot liquids. About 5 drops of the solution are used for 100 Cc. of the liquid used for titration. The solution of methyl orange contains 1 part in 1,000 parts of water. That of the base 1 part in 200 parts of alcohol.

DIPHENYL-AMINE, $(C_6\,H_5)_2\,N\,H$, is obtained by the dry distillation of aniline blue (triphenyl-rosaniline) in grayish crystals, melting at 54° C., slightly soluble in water, more soluble in acids. A 1% solution in conc. sulphuric acid (forming diphenyl-sulphonic acid) is colored intensely blue by nitric acid; also, temporarily by nitrous acid, fading to greenish yellow; also, somewhat less intensely by hypochlorous, bromic and iodic acid; to some extent by chromic, vanadic, permanganic, molybdic and selenous acid, some ferric salts, barium and hydrogen dioxide. A red color is produced by chloric acid. Ozone colors the alcoholic solution of diphenylamine, or papers stained with it, yellow to brown. It is principally employed to detect small quantities of nitric acid in sulphuric acid and nitrates in drinking water, also in wine or milk diluted with well water containing nitrates. The blue color is so intense, that 1 part of nitric acid can be shown in 3,000,000 of water, if to 1 Cc. of water a few drops of the solution are added and then 1 Cc. of conc. sulphuric acid, so as to form a layer beneath the water. The zone of contact is colored blue. The color disappears by addition of stannous salts. Hence, the quantity of nitric acid may be volumetrically determined, according to *Longi*, by using a $\frac{1}{10}$ normal solution of stannous potassium sulphate with diphenyl-amine as indicator.

EOSIN, $K_2\,C_{20}\,H_6\,Br_4\,O_5$, or tetrabromfluoresceïn-potassium, is a phthaleïn color, forming red crystals, soluble in 2 parts of water with a deep yellowish-red color. In dilution the color is reddish-yellow by transmitted light, showing green fluorescence by re-

flected light. Addition of acids destroys the fluorescence and precipitates the color, leaving a colorless liquid. Alkalies restore color and fluorescence. It has been especially recommended for titration of soap (*Fleischer*).

Ethyl Orange, one of the azo colors, in composition and uses very similar to *methyl orange*, see above *dimethyl-amido-azo-benzol-sulphonic acid*.

EUPITTONIC ACID, $C_{19} H_8 (O C H_3)_6 O_3$ (Hexa oxymethyl-aurin, Reichenbach's Pittakal). Long orange needles, obtained during the manufacture of creasote by oxidation of beechtar oils. It is slightly soluble in water or alcohol. The solution is colored *blue* by alkalies, *brownish-yellow* by acids.

Ferric alum, used as indicator for rhodanates, see *iron compounds*.

FLAVESCIN, obtained by dry distillation of oakwood at low temperature; soluble in ether, alcohol and water; the yellow solution is rendered *colorless* by acids, and *yellow* again by alkalies (Lux).

FLUORESCEÏN, $C_{20} H_{12} O_5$, is the anhydride of resorcin-phthaleïn, made by heating to 195—200° C. a mixture of 7 parts of resorcin with 5 parts of anhydrous phthalic acid, and purifying by solution in sodium hydrate and precipitation by sulphuric acid. It dissolves in alcohol with *orange-red* color and *green fluorescence*, which disappears on addition of acids. It is especially suitable for the titration of dark colored gas waters, etc., in which a color change can not be observed, while the disappearance of fluorescence is sharply marked. It is kept in the very dry state. When needed, a few crystals are dissolved in alcohol, the solution diluted with water and added to the gas liquor until fluorescence appears plainly.

FUCHSINE or ROSANILINE HYDROCHLORATE, $C_{20} H_{19} N_3 . H Cl$ (Triamido-diphenyl-tolyl-carbinol). The crystals have a green metallic lustre and transmit red light. They are slightly soluble in water, readily in alcohol with a crimson red color, insoluble in oils. Addition of acids changes the color to yellow; great dilution with water or neutralization by alkalies restores the color; ammonia and caustic alkalies also discharge to color of the aqueous solution. Hence, Fuchsine has been tried as an indicator, but is unsatisfactory. It is used to detect alcohol as an adulteration of essential oils, being insoluble in the oils, but soluble in alcohol, its dissolving in and coloring the oil shows admixture of alcohol. Fuchsine, dissolved in glacial acetic acid, is used as a

delicate reagent for nitrous acid (nitrites), whose presence changes the original crimson color, successively, to violet, then blue, green, yellow and finally to orange. Dilution with water does not restore the original color; nitric acid does not produce the color changes.

Fuchsine-sulphurous acid is a delicate reagent for aldehydes and some of their derivatives (it reacts with chloral, but not with chloral hydrate). It is prepared by passing SO_2 into a dilute solution of fuchsine in water until the color has changed to a pale yellow. The reagent may be preserved without change in well-closed bottles. The addition of a small quantity of an aldehyde produces an intense violet-red color.

Fuchsine Paper. When paper is dipped into a solution of fuchsine, rendered yellow by sulphuric acid, and dried, it becomes a sensitive indicator of ammonia gas, which colors it red.

GALLEÏN, or Pyrogallol-Phthalein, $C_{20}H_{10}O_9$, is obtained by heating for some hours an intimate mixture of 1 part of anhydrous phthalic acid with 2 parts of pyrogallol to 190° to 200° C. The fused mass is dissolved in strong alcohol and precipitated by water. It is a brown crystalline powder, with green metallic lustre, almost insoluble in cold, and but slightly in hot water; alcohol dissolves it with dark red color. In alkaline hydrates it dissolves with red color as long as it is in excess; with excess of alkali the color is *deep blue*, or in dilution, *violet*. Acids change the color to a pale yellow. It is a suitable indicator for ammonia, as well as for the fixed alkaline hydrates, carbonates and dicarbonates, for carbonic acid does not affect it. It indicates organic acids well and for their titration is preferable to methyl-orange (*Dechan*).

GENTIANA VIOLET, crystals of pale green metallic lustre, easily soluble in water with *violet* color, which is unchanged by alkalies, but indicates small traces of acids by turning *blue* (or green with greater excess). It is much used for staining of micro-organisms, urinary casts, etc.

GEORGINA or DAHLIA. The petals of the dark violet varieties yield to alcohol and water a coloring matter (anthocyanin), which, like that of coleus or red cabbage leaves, is colored *green* by alkalies, *red* by acids. It is often used in the form of paper impregnated with the tincture.

GUAIACUM, TINCTURE AND PAPER. The freshly prepared tincture and paper is turned blue by ozone, and, therefore, serves to detect ozone and various substances capable of setting it free. When added to urine containing pus, the blue color is produced. In conjunction with oil of turpentine, or ether containing hydrogen

dioxide, it has been used to detect blood. Hydrocyanic acid turns blue a mixture of guaiacum and copper sulphate, and freshly prepared guaiacum-copper paper can detect very small quantities. On the other hand, a mixture of guaiacum and very dilute solution of potassium cyanide detects traces of copper by the blue coloration.

The tincture, as well as the paper, soon lose their sensitiveness by keeping, and must, in case of doubt, be tested with a specimen known to contain ozone, or hydrocyanic acid, to see whether they yet promptly produce the blue color. It is best to prepare them fresh immediately before use.

Clean pieces of the crude native resin are selected in preference to the refined (which has been exposed to air, etc., by the purifying proeess), or else the inner portion of a larger piece of guaiacum wood (lignum vitæ). Three parts of resin (or 12 parts of wood) are digested with 100 parts of alcohol and the clear tincture decanted; air and light being excluded, as far as possible. The paper is made by steeping into this tincture a *paper free from wood pulp*, as the latter often turns blue spontaneously. If copper is to be added, the paper is first dipped into the guaiac tincture, dried quickly to remove alcohol, and then dipped into a solution of one part of copper sulphate in 1,000 parts of water, and applied immediately to the mixture to be tested for hydrocyanic acid.

Helianthin, also called Poirier's Orange III, Methyl Orange or Tropæolin D, see *dimethyl-amido-azo-benzol-sulphonic acid*, page 20.

INDIGO. Commercial indigo contains a variety of ingredients, of which *indigo blue* or *indigotin*, $C_{16}H_{10}N_2O_2$, is the most important. This is insoluble in water and alcohol, soluble in concentrated sulphuric acid, forming mono and disulphuric acids. The alkali salts of the latter (sulph-indigotic acid), sold as indigo-carmine, are soluble in water. Indigo solution, as well of the acid as its salts, is of deep blue color, and is used as a qualitative reagent for nitric acid, chlorine and its oxygen acids, which oxidize and convert it into isatin-sulphonic acid, thereby changing the deep blue color into yellow. The solution is prepared either by dissolving 1 part of indigo-carmine in 150 parts of water, or by gradually stirring 1 part of finely powdered indigo into 6 parts of fuming sulphuric acid, contained in a vessel well cooled, to prevent the destruction of indigotin by heat. The mixture is set aside for some days and then poured into 120 parts of water, well mixed and then filtered.

This solution is also used in *Mulder's* test for glucose in urine. The urine is colored by a few drops of indigo carmine, sufficient

sodium carbonate is added to render the mixture alkaline, and then a gentle heat applied. If glucose be present, the blue color changes first to green, then to a purplish red and at last to yellow. Shaking vigorously with air restores the blue color.

It also serves as an indicator for volumetric determination of caustic alkalies in the presence of carbonates. The solution for this purpose is made by treating 1 part of indigo with 6 parts of fuming sulphuric acid for several days, just as above described, then adding calcium carbonate to neutralize, diluting with 10 parts of water and filtering. The blue solution is not affected by alkaline carbonates, but turns yellow with caustic alkalies. A few drops are added to the alkali solution to be tested, and acid is added until the yellow color changes to blue (*Engel and Ville*).

An empirical standard solution for the volumetric determination of nitric acid in small quantities, especially nitrates in drinking water, is made by diluting solution of indigo (or of pure indigotin) so that it corresponds to a solution of pure potassium nitrate in water, containing 0.1607 grammes in 1 litre (= 0.1 gr. $H\,N\,O_3$). This solution is so adjusted that when 10 Cc. of the indigo solution are added to 10 Cc. of the nitrate solution, mixed with 10 Cc. of pure conc. sulphuric acid, while yet hot, the last drop must communicate a permanent greenish-blue color. The results are reliable only when equal conditions of temperature, rapidity of mixing, etc., are scrupulously observed in standardizing and in actual analysis. Each cubic centimetre of indigo solution used to produce the permanent color indicates 0.1 milligramme of $H\,N\,O_3$. Others make standard solutions of different strengths: 1.8724 grammes of $K\,N\,O_3$ to 1 litre, each Cc. corresponding to 1 Mgr. $N_2\,O_5$ (*Marx*, *Trommsdorff*, etc.); or 0.0962 gr. $K\,N\,O_3$ = 0.06 gr. $H\,N\,O_3$ in 1 litre (Mayrhoffer).

LACMOID, $C_{12}\,H_9\,N\,O_4$. A resorcin derivative, owing its name to its similarity to litmus (lacmus), which, however, it greatly exceeds in delicacy. It is made by gradually heating to 110° C., on an oil bath, a mixture of 20 parts of resorcin (meta-di-oxy-benzol) with 1 part of sodium nitrite and 1 part of water, contained in a capacious flask. A violent reaction ensues, during which ammonia is evolved and the color changes from yellow to blue. The mass fuses, and, after cooling, is dissolved in a small quantity of water. To the blue solution hydrochloric acid is added, which precipitates the lacmoid; this is separated on a filter, washed and dried, forming a red-brown, friable mass. It dissolves readily in alcohol, slightly in water, with a deep wine-red color, which is changed to *blue* by alkalies, and restored [to *red* by acids. It is a delicate

indicator for the hydrates, arsenites and borates of alkalies and alkaline earths and for inorganic acids. Solutions of zinc, cupric and ferric chlorides and sulphates, which redden litmus, leave lacmoid unchanged, unless they contain free acid. The solution is made by dissolving 1 part of lacmoid in 200 parts of dilute alcohol. Paper is impregnated with a still weaker solution. One drop of ammonia water in 5 litres of water suffices to produce the blue color (*Traub and Hock*).

LITMUS or LACMUS. In commercial litmus there are contained azolitmin, erythrolitmin, spaniolitmin and erythroleïn, combined with ammonium, potassium and calcium, and mixed with a considerable amount of gypsum, carbonate of calcium, etc. For very sensitive work *azolitmin* is isolated and its pure solution used. See page 47. Most of the other ingredients which interfere with delicate reactions may be removed and a good solution obtained by exhausting coarsely powdered litmus with boiling strong alcohol, so dissolve out the erythrolitmin. The residue, in which alkalies still preponderate, is then digested with an equal weight of water, and the solution drained off. This may be used for making ordinary blue litmus paper, but is too alkaline for delicate indications. The residue is now digested with five parts of boiling water, and the filtered solution, which contains mostly azolitmin, is preserved in wide-mouth bottles, closed with a plug of cotton, so as to exclude dust but admit air, for in closely stopped bottles the solution soon deteriorates.

To make *blue test paper*, unsized white paper, free from wood pulp, but not too porous, is dipped into the solution, and dried by suspending on strings of clean twine. For *red paper* a very small quantity of hydrochloric acid is added to the solution before dipping, so as to barely turn the color red.

Litmus solution and paper turn *blue* with alkalies, *red* with acids and many metallic salts. By lamplight the color change is not easily observed, unless the yellow sodium flame be used. Carbonic acid gives an intermediate violet color, dicarbonates do not affect the color. Hence, it is suitable for titration of the hydrates of alkalies and alkaline earths, alkaline silicates and arsenites, and for free sulphuric, hydrochloric, nitric and oxalic, somewhat less for acetic acid. In the titration of carbonates heat must be called in aid to decompose dicarbonates and expel carbon dioxide.

LOGWOOD and HÆMATOXYLIN, $C_{16}H_{14}O_6$. An aqueous solution of hæmatoxylin is used to detect alum in bread by assuming a blue color. Also, in the titration of the carbonates of alkaline earths or other alkalies, with which it turns of a *violet-blue*

color, which acids change to *yellow*. Instead of the solution of pure hæmatoxylin, the yellow inner part of a larger piece of logwood may be extracted with pure boiling water. The violet solution is turned yellow by a drop of very dilute hydrochloric acid.

Paper, previously freed from lime by dilute acid and washing, is stained yellow with this solution and forms a delicate indicator for ammonia, which turns it blue or blue-black, also for other alkalies. It must be preserved in closely stoppered bottles.

MALVA. The petals of malva rosea and other dark red varieties yield to dilute alcohol a color similar to, if not identical with that of georgina, which turns *green* with alkalies, *red* with acids. They are often used for fraudulent manufacture of red wine.

Mesityl-quinone is a rather improper name for a substance whose yellow solution in ether is colored violet by alkalies.

Methyl-orange, the same as Helianthin, Tropæolin D, or Orange III. See *Dimethyl-amido-azo-benzol-sulphonic acid*, page 78.

METHYL-VIOLET or Pentamethyl-parafuchsin, $C_{19}H_{12}N_3(CH_3)_5 \cdot HCl$, is made by oxidation of dimethyl-aniline with cupric nitrate and sodium chloride. It forms crystals of gold-green lustre, easily soluble in alcohol and in water with violet color. Addition of a small quantity of a mineral acid changes the color to blue, a larger amount to green. In very dilute solution it serves in clinics to detect traces of hydrochloric acid in gastric juice. It belongs to the group named "basic colors," by Ehrlich, and is used for staining of micro-organisms, urinary casts, etc.

It also serves to detect fusel-oil in spirits. The alcohol is mixed with an equal volume of ether, and then diluted with sufficient water to render the ether insoluble. The ethereal layer floats on top and holds the fusel-oil (amyl alcohol) in solution. It is then separated and thoroughly shaken with a solution of 1 part of methyl violet in 100 parts of water, to which enough of very dilute (2%) hydrochloric acid has been added to render it green. The mixture is poured into a graduated cylinder, and the ether left to evaporate spontaneously, so as to concentrate the solution of fusel-oil. As soon as the ether has evaporated, so as to contain 2% of amyl alcohol a blue color will be communicated to it, and by using a measured volume of spirits the quantity can be determined (*Uffelmann*). If bile be present in urine and a few drops of the solution of methyl-violet are added, the color turns a carmine-red (Paul). As acetic acid does not change its color, the presence of even minute quantities of mineral acids in vinegar may be detected by the blue color of a dilute methyl-violet solution when a drop of adulterated vinegar is added to it.

Nessler's test for the colorimetric determination of ammonia is an alkaline solution of mercuric potassium iodide. See *Mercury and its Compounds.*

p NITROPHENOL, $C_6H_4.NO_2OH$ (1 : 3), colorless crystals, soluble in much water. The color is turned yellow by alkalies; hence, its occasional use as indicator. Prepared by gradual addition of 1 part of phenol to 6 parts of ice cold dilute nitric acid of spec. gr. 1.12 (20%). A dark oily liquid separates, which consists of ortho and para-nitrophenol. These are separated by distilling with superheated steam at 214° C., when the ortho-compound distills over while the para-nitrophenol remains as residue, and is further purified by converting into the yellow sodium salt, crystallizing, separating by acid and distilling.

ORANGE PEEL. An ethereal tincture of fresh orange peel becomes colorless with acids and bright yellow with alkalies; it may, therefore, in case of necessity, serve as indicator (*Bouchardat*).

Petri and Lehmann's indicator is made by mixing 5 Cc. liquid phenol with 5 Cc. conc. sulphuric acid, adding to it, drop by drop, a solution of 1 gr. potassium nitrite in 20 Cc. concentrated sulphuric acid, and heating to 80° C. until the color has become a dark blue-violet, and continuing the heat for some time after. The mixture is then poured into two litres of cold water, when the indicator separates as a violet insoluble mass. This is washed, dissolved in ether, the solution filtered and the ether distilled off. The residue is dissolved in alcohol. With dilute acids the color is *orange-red*, with alkalies, *violet-blue*. Concentrated sulphuric acid turns it blue.

PHENACETOLIN, introduced by *Degener* for the purpose of determining at a single titration the amount of hydrate of alkalies or alkaline earths and that of their carbonates. The indicator is prepared by heating for several hours 20 parts of conc. sulphuric acid with 17 parts of phenol and 12 of glacial acetic acid, until a resinous looking residue remains. This yields to boiling water a brown solution of phenacetolin, while a greenish mass remains undissolved. The filtered solution may be used directly or evaporated to dryness for preservation. It is more soluble in alcohol than in water. The solution, when strongly diluted, is rendered *pale yellow* by alkaline hydrates, *deep red* by carbonates and *golden yellow* by acids. When a mixture of caustic alkali and carbonate is titrated with sulphuric acid the specimen solution is tinted with a few drops of phenacetolin until pale yellow, as soon as enough acid is added to neutralize the hydrate, the color changes to red from the remaining carbonate, and turns a deep golden-yellow

with the first drop of acid in excess. The indicator also serves for alkaline silicates and arsenites.

PHENOL-PHTHALEIN, $C_{20} H_{14} O_4$. This is one of the most sensitive indicators known, on account of the difference of its color reactions, passing from deep *purplish-red* for alkalies to *colorless* for acids with great promptness and without intermediate tints. It is suitable for most acids and acid salts, for alkaline hydrates and carbonates, but is not adapted to ammonia or dicarbonates. It is prepared by mixing 10 parts of melted phenol with a solution of 5 parts of anhydrous phthalic acid in 4 parts of conc. sulphuric acid, and keeping them for a whole day at the temperature of 120° C. The fused mass is then poured into boiling water, and the excess of phenol and of phthalic acid is removed by repeated change of boiling water. The undissolved residue is then dissolved in a dilute solution of caustic soda, filtered and precipitated by acetic acid, to which a little H Cl has been added. After 24 hours, the phenol-phthalein has subsided and is separated from the solution. When dried it forms a brownish-gray mass, which may be used in its as yet somewhat impure state, or purified by treatment with animal charcoal, etc.

A solution of 1 part in 100 parts of alcohol, of about 50%, serves as indicator, of which 2 drops suffice to color 100 Cc. of liquid. In pure water it produces a slight milky turbidity, and remains colorless with most soluble salts and free acids, but turns a deep purplish-red on the slightest excess of alkaline hydrate or carbonate or caustic alkaline earths; dicarbonates leave it colorless.

m Phenylene-diamine. See page 78, *m Diamido-Benzol* in this article.

PHLOROGLUCIN, $C_6 H_3 (O H)_3$, isomeric with pyrogallol. It is used to detect minute quantities of free acid, especially for the clinical examination of gastric juice for free hydrochloric acid. For this purpose dilute solutions of *phloroglucin* and *vanillin* are mixed, and a drop or two added to an equal amount of the gastric juice. If even as little as 0.025% of H Cl is present, the mixture slowly reddens as it dries (*Guenzburg*). The color change is not prompt enough to allow its use as volumetric indicator. It also serves to detect cane or grape sugar by turning an orange color when gently heated with them. In microscopical research it serves to stain woody fibre; it may also be used to detect wood pulp in paper, by staining it violet-red when brought together with it in acidulated alcoholic solution and heated; pure linen or cotton paper is not affected (*Wiesner*).

Phloroglucin may be prepared from phloretin, phloridzin, guercetin, maclurin and other substances by melting them with alkaline hydrates. Its principal source is the *maclurin*, obtained as a bye-product in the manufacture of the yellow dye from fustic (morus tinctoria). On a small scale it can be made by melting 1 part of resorcin with 6 parts of sodium hydrate, until the evolution of gas ceases and the fused mass has assumed a chocolate brown color. This is then dissolved in acidulated water, and the phloroglucin extracted by shaking with ether. The impure phloroglucin left on evaporation of the ether is heated to 100° C., to remove any unchanged resorcin, and then purified by repeated crystallization.

Poirrier's Blue, C_4 B, a rosaniline derivative is sometimes used in alcoholic solution as indicator for even feeble acids, which do not respond to methyl-orange or phenol-phthalein. It turns *red* with alkalies, *blue* with acids. Borax manifests acid reaction with it.

Rhubarb. Its tincture is used to stain paper, which turns *yellow* with acids, *brown-red* with alkalies.

Rosolic acid, see page 19.

SODIUM SALICYLATE, $(Na\ C_7\ H_5\ O_3)_2 + H_2\ O$, is used as an indicator for the titration of ferric salts by sodium hyposulphite. The violet color it produces with ferric salts turns colorless at the completion of the reduction (*Haswell*).

The commercial salt is of sufficient purity. See also *Salicylic Acid*, page 19.

TEST PAPERS. These are used in narrow strips for ascertaining neutrality, either by dipping into the liquid or by placing upon them a drop by means of a glass rod. In some cases of volumetric analysis they are employed in preference to adding the color reagent to the solution. The paper used in their preparation should be unsized, so as to permit the ready entrance of the color to the fibre, yet not too loose in texture so as to absorb too readily. A pure, unsized rag paper, linen or cotton, is to be selected, free from admixture with wood pulp, which interferes with some reactions. Filter paper is mostly too porous in structure. The paper is cut into sheets of suitable dimensions, which are impregnated with the color solution (litmus, turmeric, red cabbage, phenol-phthalein, etc.), either by dipping or by the application of a soft flat brush. The moist sheets are hung up to dry on strings of white thread, preferably in a dark room. After drying, they should be preserved in dark wrappers. It is very convenient to glue them together at one end before cutting into narrow strips, so as to have them in book form.

TETRA-HYDRO-ELLAGIC ACID, $C_{14}H_{10}O_8$, called also *hydrorufigallic acid*, when melted with potassium hydrate, is converted into an isomeric body as yet unnamed, which is recommended by *Oser and Kahlmann* as a sensitive reagent, especially for carbonates, which react with it as if no carbonic acid were present.

Hydrorufigallic acid is prepared by adding potassium permanganate to a solution of gallic acid in very dilute sulphuric acid. The product is extracted by shaking out with ether, evaporating and crystallizing from alcohol. One part of the crystals is fused with 5 parts of potassium hydrate until the mass turns red-violet. It is now saturated with sulphuric acid, which leaves an insoluble greenish-yellow substance, which is purified by crystallization from boiling water. It is now dissolved in dilute potassium hydrate solution. The color, until neutralized, remains olive-green, but on the slightest excess of alkali becomes intensely red. When the red substance is diluted and accurately neutralized with sulphuric acid it forms the indicator. Any excess of acid colors it *yellow;* alkalies, *red.* Not only the carbonates of alkalies, but of alkaline earths, also ferrous and manganous carbonate turn the color red, and, therefore, the indicator is valuable in titration of mineral waters, etc.

TROPAEOLIN. This name is given by manufacturers to a variety of orange dyes, which are distinguished by the affixes: O, OO, OOO I, OOO II, D and Y. All have been used as indicators and resemble, more or less, the *Tropaeolin D*, which, under the name of *Helianthin*, *Methyl Orange* has been described in this chapter as *Dimethyl-amido-azobenzol-sulphonic acid.* This appears to excel in delicacy, but the others are occasionally substituted, and produce mostly *yellow* tints with alkali, *red* with acids.

Tropaeolin O, Chrysoin or Resorcin Yellow, is meta-dioxy-azobenzol-sulphonic acid.

Tropaeolin OO, or Diphenylamin Orange, is phenyl-amido-azo benzol-sulphonic acid.

Tropaeolin OOO I, Mandarin or Orange II, is sulpho-azobenzol-beta-naphthol.

Tropaeolin OOO II, or Orange I, is sulpho-azobenzol-alpha-naphthol.

Tropaeolin Y is oxyazobenzol-sulphonic acid.

TURMERIC or CURCUMA. The root of several varieties of curcuma contains *curcumin*, $C_{14}H_{14}O_4$, which is soluble in alcohol with yellow color, changed to brown-red by alkalies. Other constituents, soluble in water, impair the delicacy of this color-change. Hence, the tincture is made by digesting one part of the powdered

root repeatedly with small quantities of water and rejecting the aqueous extract, and then digesting for several days with 6 parts of alcohol and filtering. It is seldom used directly, but serves to impregnate unsized paper, which should be dried and preserved in the dark. The color of turmeric paper is changed to brown-red by alkalies, and restored to yellow by acids, with the exception of *boracic acid*, which produces, even in the presence of hydrochloric acid, a *red* color (after drying), which serves for the detection of borates. Turmeric paper is especially useful for titration with baryta water and for colored liquids, which would hide the color of an indicator added directly. Also for organic acids, especially citric, acetic, tartaric, lactic, oxalic and succinic, but hardly for the fatty acids of oils, etc. Brown-red turmeric paper serves to detect acid in alcohol.

VANILLIN, $C_8H_{10}O_3$, the methyl ether of protocatechuic aldehyd, forms the crystalline covering of vanilla beans. It is purified by recrystallization from boiling petroleum-ether. Dissolved in dilute hydrochloric acid, it is used especially in microscopic research as a reagent for phenols, with which it produces a red color. Not all phenols react with equal promptness. A solution containing one part of vanillin, dissolved in 100 parts of alcohol, to which 100 parts of water and 600 parts of hydrochloric acid are added, reddens, in dry microscopic sections, only phloroglucin and orcin, while pyrocatechin, cumarin, resorcin, phenol, salicylic acid, pyrogallol, etc., etc., are not affected, but require a more concentrated solution.

Mixed with *phloroglucin* in dilute solution it serves to detect minute quantities of acid (hydrochloric acid in gastric juice). See *phloroglucin* above, page 87.

Wurster's papers for ozonometry, see *p amido-dimethyl-aniline*, page 43. The tetra-methyl paper gives with ozone a blue color, the di-methyl paper a red.

Congo-red and *Congo-paper*, see *Color Reagents and Indicators*, page 77.

COPPER AND ITS COMPOUNDS.

COPPER, Cu.

USES. In the metallic state copper is employed in qualitative analysis, in the form of bright, polished foil or wire, for the reduc-

tion of arsenic by Reinsch's method, and for the detection of the salts of mercury, by reduction to metallic quicksilver. Occasionally it serves to detect nitric acid by its reduction to a lower oxide. It is also used to reduce stannic chloride to stannous. In elementary organic analysis of nitrogenous bodies it is used to deoxidize nitric oxide and reconvert it to nitrogen. The form used for this purpose is either a bundle of copper turnings, a spiral of thin wire, a roll of thin foil or of wire webbing, or asbestus coated with fine copper (see page 47). For nearly all these purposes a good commercial article is sufficiently pure, and care must only be taken to have a perfectly clean surface, but in forensic examination for arsenic the metal must be absolutely free from arsenic, and for the preparation of copper amalgam a perfectly pure metal is necessary. Atomic weight of Cu = 63.173.

TESTS. Iron, manganese, nickel, lead, silver, tin, bismuth, antimony and arsenic are often found in copper, when made by the furnace process, while the cement copper, prepared by precipitating the solutions by iron, is only liable to contain the latter metal, and copper, made by the recently introduced electrolytic process, is absolutely pure, and should be used for chemical purposes to the exclusion of any other.

To test for arsenic, a small quantity of copper is boiled with sulphuric acid and the solution tested by Marsh's process in a suitable apparatus for evolving and igniting the hydrogen. To examine for other impurities, the metal is dissolved in nitric acid, in which it must leave no residue; a small portion of the solution is tested with sodium chloride or hydrochloric acid, and must give no precipitate (absence of silver and bismuth). The rest of the solution is precipitated by pure sodium hydrate, and the cupric hydrate well washed on the filter. Filtrate and washings must give no precipitate with hydrogen sulphide (abs. of lead, zinc). The precipitated cupric hydrate is redissolved in dilute sulphuric acid, and, after the copper has been precipitated by electrolysis upon a platinum electrode, the acid solution must remain perfectly clear, and, on heating upon platinum foil, must leave no residue.

PREPARATION. Either by electrolytic reduction of pure copper sulphate or by reducing pure cupric oxide by heating in a current of hydrogen. The wire, turnings or rolls of foil, for use in organic analysis, must be first heated in air to destroy organic dust, and then freed from the oxide superficially formed by ignition in hydrogen.

Copper Amalgam is sometimes used in connection with hydrobromic acid for reducing sulphides, converting sulphur into hydrogen sulphide. It is made by superficially coating pure copper in

powder with mercury by rubbing it together with a small quantity of mercuric nitrate solution, washing the product and then incorporating it, under hot water, with a proper amount of pure mercury.

CUPRIC ACETATE, $Cu(C_2H_3O_2)_2 + H_2O$.

USES. Neutral cupric acetate in aqueous solution is reduced by glucose at ordinary temperature, after some hours, to cuprous oxide. This occurs more rapidly if to the solution about 1% of acetic acid is added, and the mixture boiled for a short time and then set aside. These reactions serve to distinguish glucose from cane sugar, which does not reduce at ordinary temperature; from dextrin, which does not reduce the boiled acidulated solution, and partly from milk sugar, which only reduces in very concentrated solutions (*Barfoed*).

Mol. W. = 198.133.

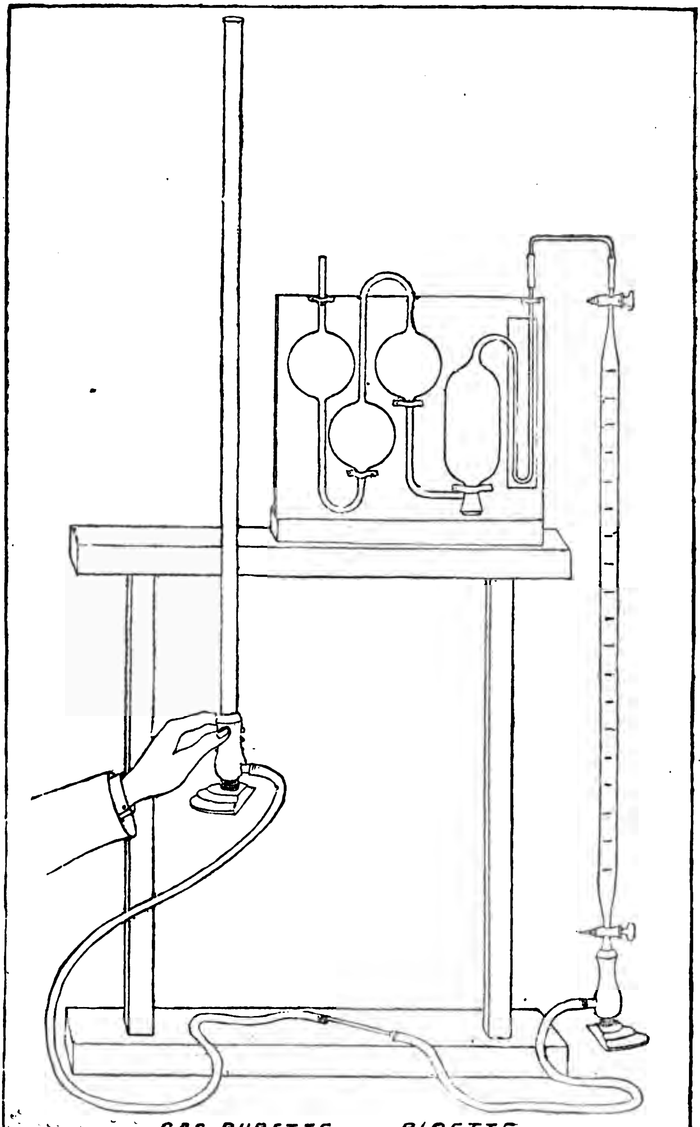
Basic cupric acetate, or *sub-acetate*, $Cu(C_2H_3O_2 . Cu(OH)_2 + 5 H_2O$, is proposed as a reagent for albuminoids, which, in presence of caustic alkalies, reduce it to cuprous oxide (Palm).

TESTS. When used for detection of glucose only, the commercial salt is of sufficient purity. In rare cases the purest salt is required. Pure cupric acetate forms opaque, deep green, clinorhombic crystals. At 15° C. it is soluble in 13.4 parts of water, and in 135 parts of alcohol of spec. gr. 0.830, at 100° C. in 5 parts of water, at 70° C. in 14 parts of alcohol. Its aqueous solution should not yield a precipitate with barium chloride; nor, after addition of nitric acid, with silver nitrate. After ignition no soluble substance should be extracted by water. A saturated aqueous solution of ammonium carbonate must dissolve it without residue. After precipitation by H_2S, the filtrate must leave no residue on evaporation. After complete precipitation by potassium or sodium hydrate, the filtrate must yield no precipitate with H_2S.

PREPARATION. By saturation of pure cupric oxide with pure acetic acid and crystallizing. The commercial salt may be purified by repeated recrystallization from hot water or alcohol. Below 8° C. small rhombic crystals with $5 H_2O$ are formed, above 8° C. the ordinary large clinorhombic crystals with 1 molec. H_2O. If the solutions are kept at boiling heat basic acetate precipitates, while acetic acid volatilizes.

CUPRIC BUTYRATE, $Cu(C_4H_7O_2)_2 + 2 H_2O$.

USES. To detect adulteration of oil of lemon by turpentine. Pure oil of lemon, when heated to 172° C., dissolves a small quantity of dry cupric butyrate, forming a clear green solution; if oil of



GAS BURETTE and PIPETTE.

Charlotte S Curtiss Del

turpentine is present, the mixture becomes turbid by separation of yellow cuprous hydrate (*Heppe*).

PREPARATION. A concentrated solution of butyric acid in water is digested with an excess of pure cupric oxide or hydrate. The filtrate, on evaporation, forms monoclinic crystals.

CUPRIC POTASSIUM CARBONATE, $Cu\,K_2(C\,O_3)_2 + 3\,H_2\,O$.

Soldaini's Reagent.

USES. This salt, dissolved in an excess of potassium dicarbonate solution, is used as a very delicate reagent for glucose, etc., especially for the detection of invert sugar in cane sugar, or glucose in urine. It is reduced to cuprous oxide by dextro-glucose, levulose, milk sugar, tannic and formic acid, but remains unaffected by cane sugar, dextrin, starch, tartaric and uric acid, and by any of the constituents of normal urine. In testing for invert sugar, 9.3 gr. cane sugar are dissolved in sufficient water to make 15 Cc. and added to 50 Cc. of Soldaini's solution previously heated. The heat is then continued for five minutes, when the reduction will be complete if invert sugar was present in the amount of 0.5 milligrammes or more. In testing urine not more than half a volume must be added to one volume of the reagent. As it keeps well without decomposition, it is one of the best reagents for use in clinics.

PREPARATION. Fifteen gr. freshly precipitated basic cupric carbonate, $Cu\,C\,O_3\,.\,Cu\,(O\,H)_2$ (prepared by precipitating a solution of 33.96 gr. pure crystals of cupric sulphate by an excess of sodium or potassium carbonate) are dissolved in a solution of 416 gr. of potassium dicarbonate in 1,200 Cc. of water, and then water added to make 1,400 Cc. If any portion remains undissolved, the solution must be filtered.

CUPROUS CHLORIDE, $Cu_2\,Cl_2$.

USES. In gas analysis cuprous chloride, in acid solution, serves to absorb carbon monoxide, acetylene, ethylene and phosphine, and in ammoniacal solution, also, some of the homologues of ethylene. This is either done by introducing into the absorption tube a ball of paper pulp soaked in a saturated solution of cuprous chloride in hydrochloric acid (*Bunsen*), or by placing this solution directly into the gas pipette (*Winkler*), or by using in the same manner an ammoniacal solution of cuprous chloride, which has greater absorbing power than the acid solution (*Hempel*). For the absorption of oxygen it is not so well suited as its action is too slow.

Preparation. Cuprous oxide is first made by heating a solution of cupric sulphate with sodium hydrate and glucose in some excess. This is added to concentrated hydrochloric acid in a well-closed flask until no more is dissolved. Or 10.3 gr. cupric oxide are mixed with 200 Cc. of concentrated hydrochloric acid, and the solution poured into a flask filled with copperwire or turnings, closed well to exclude air and digested until the solution becomes colorless. The ammoniacal solution is made by pouring the above colorless acid solution into a beaker containing 1,500 Cc. of water. The cuprous chloride, being insoluble in dilute acid, precipitates. After settling, the liquid is decanted, and the cuprous chloride, together with 150 Cc. of water, is transferred to a flask closed with a doubly perforated cork and tubes, through which ammonia gas is passed until the salt is nearly all dissolved. This solution is diluted to 200 Cc. and preserved in a close flask. It is capable of absorbing 6 Cc. of carbon monoxide.

CUPRIC HYDRATE, $Cu(OH)_2$.

Uses. Cupric hydrate, either freshly precipitated or carefully preserved in close vessels, becomes, by the presence of glycerin, soluble in a solution of sodium or potassium hydrate, and serves to determine glucose by means of a standardized solution containing 13.516 gr. of $Cu(OH)_2$ in 1 litre, corresponding to 34.635 gr. of $CuSO_4 + 5H_2O$ in Fehling's solution, and, like it, requiring 5 gr. of anhydrous glucose for complete reduction (*Loewe*). $Cu(OH)_2 =$ 97.093.

Preparation. As cupric hydrate, when well prepared and carefully preserved, will keep unchanged for many years (*Loewe*), it may be made in some quantity and stored for use, or the requisite quantity may be freshly precipitated, when needed, from the corresponding amount of pure crystals of sulphate. To prepare it for keeping 50 gr. of cupric sulphate are dissolved in 200 Cc. of water, 40 Cc. ammonia water added, and then a solution of 22 gr. pure sodium hydrate in 100 Cc. water. The precipitate is carefully washed and then dried over sulphuric acid and preserved in a close vessel.

Loewe's Solution is made by dissolving 13.516 gr. of cupric hydrate (or the fresh precipitate from 34.635 gr. of $CuSO_4 + 5H_2O$) by the aid of gentle heat in 500 Cc. water, to which 27 gr. pure glycerin and 24 gr. of sodium hydrate have been added. After cooling to 15° C. the solution is diluted to 1 litre. (Loewe directs the use of the 15.315 gr. hydrate produced by 40 gr. sulphate and dilution to 1,155 Cc., which gives the same proportions as above.)

Haines' Solution differs from the above, not only in strength, but also in not removing the alkaline sulphate produced by the precipitation of the hydrate. It uses 8 gr. copper sulphate and 9 gr. potassium hydrate, dissolved in 100 gr. glycerin and 600 Cc. water.

CUPRIC OXIDE, Cu O.

USES. In organic analysis for the oxidation of H to H_2 O and of C to C O_2, in appropriate combustion tubes. It is used either in form of fine powder or of more compact granular masses, obtained by more intense ignition, or as *asbestus coated with cupric oxide.*

In blowpipe work it serves to distinguish the halogens present in minerals or salts by the color communicated to the outer flame, when they are heated in the reducing flame with a microcosmic bead saturated with cupric oxide—chlorine, blue; bromine, bluish-green; iodine, yellowish-green (*Berzelius*). It is also used for converting the sulphides of arsenic, antimony and tin into their highest oxides, by boiling their solutions in sodium sulphide with cupric oxide, which is thereby changed to cuprous sulphide (*Berglund*). Cu O = 79.133.

TESTS. Cupric oxide must not yield anything to boiling water. When heated to a red heat no vapor must be given off, either of sulphuric, sulphurous, selenous, nitrous, carbonic or other acids, which sometimes are due to dust or vapors finding their way into open vessels when carelessly kept, or to imperfect ignition. When prepared in the dry way the fine powder is deep black and of sandy feel, the compact variety grayish-black and quite hard. That, prepared in the wet way, has a brown-black color.

PREPARATION. For the purposes of organic analysis, cupric oxide is generally made by dissolving copper in nitric acid and heating the dried nitrate to a red heat, while occasionally stirring the mass with a glass rod, until no more nitrous vapors are perceptible. After just sufficient cooling to permit handling, the oxide is ground in a clean, hot wedgewood mortar, sifted through a sieve of copper wire, and the fine powder carefully preserved from dust and vapors in closely stopped bottles. The coarser particles are reheated at a higher temperature to form the compact variety used in the combustion of more volatile substances.

Asbestus is coated, either by sprinkling with the fine powder, or better, by soaking in a concentrated solution of cupric nitrate and heating to red heat. For desulphuration the fine powder obtained as above may be used, or else it is prepared in the wet way by protracted boiling of a solution of pure cupric sulphate with a small excess of pure sodium carbonate, until the precipitate has

all been converted into oxide, then thoroughly washing and drying at 160 C.

CUPRIC SULPHATE, $Cu\ S\ O_4 + 5\ H_2O$.

USES. Cupric sulphate serves to detect bromides by forming with them, on addition of acid, a red cupric bromide. A solution of 1 part of cupric sulphate and 2¼ parts of ferrous sulphate precipitates iodides, as white cuprous iodide, from neutral solutions. In conjunction with sulphurous acid it serves to detect sulphocyanates in gas waters, etc., by a precipitate of white cuprous sulphocyanate. It is also used for precip itation of alkaline ferrocyanides, producing a deep brown-red cupric ferrocyanide; sometimes an empirical copper solution is used for their titration (*Hurter*). In a solution made slightly alkaline it forms with arsenous acid a bright yellowish-green, with arsenic acid a greenish-blue precipitate. It is also used for the detection of glucose by *Trommer's test*. On adding a small amount of cupric sulphate to the solution containing glucose, maltose, cellulose, lactose, invert sugar, etc., and then an excess of potassium or sodium hydrate, the precipitate of pale blue cupric hydrate at first formed is redissolved with a deeper blue color, and, on heating, yellow cuprous hydrate separates, which by continued boiling is converted into the red cuprous oxide. Care must be taken to use no more cupric sulphate than can be reduced by the glucose, otherwise the surplus will form black cupric oxide and interfere with the reaction. If glucose is to be detected in urine, albumen must first be coagulated by heat, and turbid urine must be filtered and, if necessary, clarified by subacetate of lead. Chloroform, chloral hydrate, tannin and other substances produce the same reaction. It also serves to detect C O in blood by the bright red color of the precipitate. Cupric sulphate is also used for the preparation of pure copper and some of its compounds, especially for making various volumetric solutions for the detection of sugars, among them Fehling's, Barreswill's, Pavy's, Haines', etc. $Cu\ S\ O_4 + 5H_2\ O = 248.797$.

Anhydrous cupric sulphate is of a pure white color, but attracts water and becomes blue; it is employed for detecting the presence of water in alcohol, etc., and for the purpose of dehydration.

TESTS. Cupric sulphate forms large, deep blue, triclinic crystals, soluble in 2½ parts of water at 15° C., in 1 part at 100° C.; insoluble in alcohol. Its acidulated aqueous solution must, after precipitation by $H_2\ S$, yield a filtrate which leaves no residue on evaporation. If into its acidulated solution bright pieces of pure iron are

immersed, and, after complete precipitation of the copper, the liquid is filtered, then heated with a little nitric acid and precipitated by ammonia in slight excess, it must, after removing the ferric hydrate by filtration, yield no residue on evaporation and ignition upon platinum foil. For quantitative purposes only clean crystals must be selected, which have not become white by superficial loss of water of crystallization.

PREPARATION. As it is very difficult to purify commercial sulphate containing other metals (excepting iron), recrystallizing is not to be depended upon for obtaining pure material, and it is best to use pure metallic copper and dissolve it in pure sulphuric acid. By boiling in a suitable flask the sulphur dioxide evolved may be utilized for making sodium di-sulphite or solution of sulphurous acid. The solution of sulphate in the flask is filtered, freed from any remaining SO_2 by heating with a little nitric acid and repeated crystallization, the first crystals forming being the purest. The pure dried crystals must be carefully preserved in well stoppered bottles to prevent loss of water.

CUPRIC TARTRATE, $Cu\,C_4\,H_4\,O_6 + 3\,H_2\,O$.

USES. In solution with alkaline hydrates for detection and volumetric determination of sugars. The principal one of these is known as

Fehling's Solution,

of which, however, a number of modifications exist. It is so adjusted that 1 litre is designed to be completely reduced to red cuprous oxide by boiling with 5 grammes of dextro-glucose, $C_6\,H_{12}\,O_6$. It is usually assumed that this reduction occurs most accurately when the glucose is used in 2% solution. Careful investigations of Soxhlet, Degener and Allihn have shown that accurate results are obtainable only when the solutions not only contain the same amount of cupric tartrate (36.702 gr. $Cu\,C_4\,H_4\,O_6 + 2\,H_2\,O$, corresponding to 34.635 gr. $Cu\,S\,O_4 + 5\,H_2\,O$ in 1 litre at 15° C.), but also the same amount of alkaline hydrate and tartrate, and when the same conditions of concentration of the glucose solution, rapidity of admixture and time of boiling are strictly complied with. By using a 1% solution of sugar, 100 Cc. of Fehling's solution require for reduction:

0.4752 gr. dextrose, time, 2 minutes.

0.5044 gr. levulose, time, 2 minutes.

0.6756 gr. lactose, time, 6 minutes.

0.7788 gr. maltose, time, 4 minutes.

0 4940 gr. invert sugar (either from cane or milk sugar), time, 2 minutes

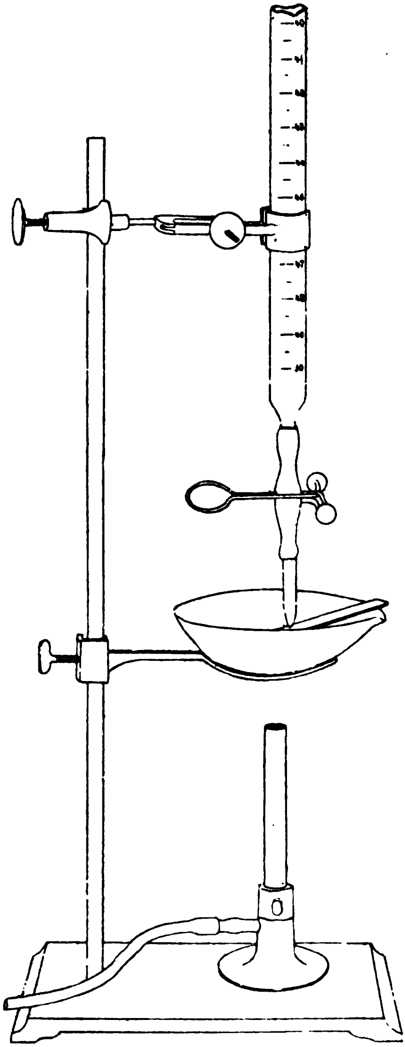
(Degener states that by the use of 18 molecules of Rochelle salt and 6 mol. of alkaline hydrate, 6 mol. of cupric salt are reduced by 1 mol. of glucose.)

Fehling's solution, as usually prepared, easily deteriorates and deposits cuprous oxide, even at ordinary temperatures, and still more by boiling, even without any addition. To prevent this, Pavy adds ammonia. Others recommend to keep separate solutions of the copper sulphate and the alkaline tartrate and hydrate and to mix them in proper proportion immediately before use. It is best in every case where accurate results are required to make a preliminary test, using 10 Cc. of Fehling's solution, and according to the results obtained to dilute the urine or glucose solution so as to contain near to 1%, and then repeat the titration with 10 Cc. (or more) of Fehling's solution, adding rapidly to it nearly the whole quantity ascertained to be requisite, and then finishing as rapidly as possible by gradually adding the rest till the reduction is complete. The end-point is ascertained by the disappearance of the blue color, or, as this in many cases is not reliable enough, by separating a drop of the hot mixture and ascertaining the presence or absence of copper by "spotting" with solution of potassium ferrocyanide, acidulated with acetic acid. A very accurate result may be obtained by using for the final determination a number of flasks containing the same amount of Fehling's solution. To the first one of these an amount of sugar solution is added, slightly less than that indicated by the preliminary test; to the next one a little more, and so on. After boiling, the clear liquid of the flasks is tested for copper by ferrocyanide. The true amount of sugar needed must be between that used in that last flask giving the reaction and the first one failing to do so. Some prefer to heat the sugar solution with an excess of Fehling's solution, and to weigh the reduced cuprous oxide.

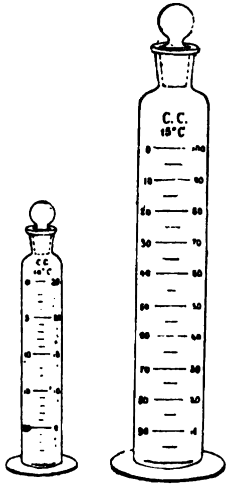
An addition of a few drops of solution of aluminium sulphate or calcium chloride or zinc chloride towards the end of the reduction facilitates the rapid deposition of the cuprous oxide and leaves the liquid clear, $Cu\,C_4\,H_4\,O_6 + 3H_2\,O = 264.709$.

Tests. Fehling's solution must, on boiling for 2 minutes, either alone or diluted with water, remain perfectly clear and show neither change of color nor the slightest red deposit.

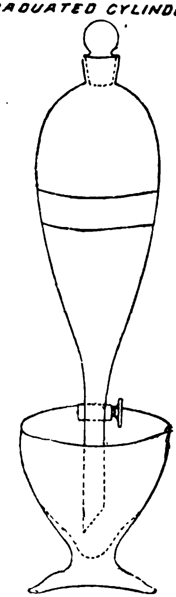
Preparation. Dissolve 34.635 gr. of cupric sulphate, in clear crystals, in distilled water, and dilute to 500 Cc. at 15° C. (or at the temperature indicated on the flask), and preserve in a well-closed glass-stoppered flask. Then 173 gr. of Rochelle salt, $K\,Na\,C_4\,H_4\,O_6 + 4\,H_2\,O$, and 125 gr. K O H (or 89 gr. Na O H) are dissolved in water, diluted to 500 Cc., and also preserved separately in a well-



APPARATUS FOR FEHLING'S TEST.



GRADUATED CYLINDERS.



HARADA'S SEPARATOR

closed bottle. The water used for solution should be boiled before use to destroy any germs of fungi, which might attack the tartrate. To avoid deterioration the tartrate solution may be made only immediately before use.

It is a useful precaution to ascertain the correctness of the titre of Fehling's solution by actual trial with absolutely pure dextroglucose, under the same conditions of concentration, time of boiling, etc., as are to be observed with the specimen to be tested. For its preparation, see *Glucose*.

In *Pavy's* modification of Fehling's solution 400 Cc. of ammonia water, of 0.88 sp. gr., are used instead of water, and the whole ingredients mixed and reduced to 1 litre.

Instead of 173 gr. Rochelle salt, *Schmiedeberg* proposes to use 16 gr. pure mannite. *Degener* precipitates the cupric sulphate by alkaline tartrate, and saturates with this a solution of caustic soda. *Barreswill*, whose solution is much used in France, uses cream of tartar, sodium carbonate and potassium hydrate to dissolve the same quantity of cupric sulphate as in Fehling's solution.

CUPRAMMONIUM COMPOUNDS.

Copper forms a large number of compounds containing 2 or 4 mol. of $N\,H_3$, according to the general formulæ: Salts of cupri-diammonium $Cu\,(N\,H_3)_2\,.\,R_2$; cupri-tetrammonium $Cu\,(N\,H_3)_4\,.\,R_2$; cuproso-diammonium $Cu_2\,(N\,H_3)_2\,.\,R_2$; cuproso-tetrammonium $Cu_2\,(N\,H_3)_4\,.\,R_2$. Of these the following are used as reagents:

CUPRI-TETRAMMONIUM HYDRATE, $Cu\,(N\,H_3)_4\,.\,(O\,H)_2$, *Schweitzer's reagent*, used, especially in microscopical investigations, to dissolve cellulose (cotton cloth, filterpaper, etc.). It is a deep blue liquid, made by repeatedly letting strong ammonia water drip slowly through fine copper turnings packed into a small cylindrical percolator, air being freely admitted (Peligot). Or by dissolving pure cupric hydrate in ammonia water. It should be freshly prepared for use, as preservation gradually impairs its efficiency.

CUPRI-TETRAMMONIUM SULPHATE, $Cu\,(N\,H_3)_4\,.\,S\,O_4 + H_2\,O$. This is used in watery solution for the same purpose as the hydrate. It also forms a precipitate of green cupric arsenite with arsenous acid. It is also used as *Kieffer's* volumetric solution for determination of acids.

The dry salt crystallizes in deep blue, rhombic prisms, soluble in 1.5 parts of water, which lose ammonia in air, and still more rapidly by heating.

It is prepared by dissolving 1 part of cupric sulphate in 3 parts of ammonia water. To the filtered liquid 6 parts of strong alcohol are added, causing precipitation of the crystals. They must be preserved in well-closed bottles. *Kieffer's solution* is prepared by dissolving cupric sulphate in water, adding ammonia until the pale blue precipitate of cupric hydrate is redissolved, and then adjusting the titre by dilution with water, so as to correspond with either normal or decinormal hydrochloric (or sulphuric) acid. The formation of a pale blue precipitate indicates the end of the reaction.

CUPRI-TETRAMMONIUM CHLORIDE, $Cu(NH_3)_4Cl_2 + H_2O$, is used for the quantitative determination of carbon in iron by the *McCreath-Ullgren* method. In this process 50 Cc. of the cuprammonium chloride solution (containing 15 gr. of the crystals) are used for every 1 gr. of iron to be tested. The iron at first precipitates the copper, dissolving in its stead, but by stirring for several minutes the precipitated copper is redissolved, forming cupricuproso-tetrammonium chloride, while all of the carbon is left behind undissolved. This carbon is carefully collected in a small filtering tube, filled with asbestus or glass-wool, and washed thoroughly, first with water, then with dilute hydrochloric acid, and at last with water. The filtering tube is then transferred to a flask connected with suitable apparatus and the carbon is oxidized by means of chromic and sulphuric acid. The resulting carbon dioxide is absorbed in a Liebig's potash-bulb and weighed.

The reagent is prepared by dissolving 160 gr. of cupric oxide in 450 Cc. of hydrochloric acid of spec. gr. 1.16. After solution and filtration the liquid is saturated with ammonia gas and left to crystallize. Of the blue octohedral crystals, of $Cu(NH_3)_4Cl_2 + H_2O$, 800 grammes are dissolved in water and diluted to 1 litre.

DIASTASE.

USES. This ferment, contained in malt, has the property to convert starch into dextrin and maltose. By heating with dilute acid (inversion) and titration with Fehling's solution, the amount of sugar, and, by calculation, that of the starch may be determined. It is principally used for determination of starch used in adulteration of food (sausages, etc.).

PREPARATION. 5 gr. of ground malt are digested at 30° to 40° C. for 1½ hours in 50 Cc. water, filtered and used at once.

Diazo-benzol-sulphonic acid, see *sulphanilic acid*, p 20.

Dimethyl-para-phenylen-diamine, see *p Amido-dimethyl-aniline*, p. 43.

Diphenyl-amine, see in chapter on *Color Reagents and Indicators*, p. 79.

Dipterocarpus Oil.

This oil, distilled from *gurjun balsam*, a substance closely allied to copaiba, is used to detect free mineral acids in presence of organic acids; 1 part of the oil, dissolved in 30 parts of glacial acetic acid, does not change color on addition of organic acids, but with the smallest traces of sulphuric, hydrochloric or other mineral acids it turns first rose-red, then deep violet The color is not discharged by alcohol (*Jorissen*).

Eosin, see *Color Reagents*, page 79.

ETHERS.

ETHYL ACETATE, $C_2H_5 . C_2H_3O_2$.

Acetic Ether.

USES. As a solvent of chloral hydrate, which it extracts from animal fluids in either acid or neutral solution. Also for the separation of alkaloids from solutions made alkaline by sodium carbonate. For this purpose it must be free from admixture with alcohol. An equal volume of the alkaline liquid containing the alkaloid and of acetic ether is thoroughly shaken together, and, after separation, the ethereal layer containing the alkaloid is removed. To it acidulated water is added, which renders the alkaloid salt insoluble in the ether, but soluble in water. For purification the process is repeated. It is especially applicable to morphine, strychnine, brucine, etc., less so to the cinchona alkaloids (*Barfoed*).

TESTS. Pure acetic ether is a colorless, volatile liquid of fruity odor; specific grav. at 0° C. = 0.9051, at 15° C. = 0.8981; it boils at 72.78° C. It is miscible in all proportions with alcohol, ether and chloroform. At 17.50° C. 1 part requires 17 parts of water for solution; while 28 parts of acetic ether dissolve in 1 part of water. Its reaction with test papers is neutral, when well preserved from air and light, otherwise it is liable to contain free acetic acid. For analytical purposes the presence of alcohol is especially to be guarded against; hence, when 10 Cc of the ether are shaken with an equal volume of pure water in a graduated cylinder; well-stoppered, and set aside to separate the upper ethereal layer, must, at 17.5° C., occupy a volume of at least 9.3 Cc. A greater shrinkage from solution in the water indicates too much alcohol.

PREPARATION. To a mixture of 26 parts of conc. sulphuric acid with 12.5 parts of 94% alcohol 20 parts of anhydrous sodium acetate are gradually added and the mixture distilled on a water-bath. The product is purified by shaking at first with some dry sodium carbonate, then with fused calcium chloride, and, lastly, redistilling below 76° C.

ETHYLIC ETHER $(C_2H_5)_2O$.

USES. Pure ethylic ether, usually called *ether*, is used as a solvent for a variety of substances, inorganic and organic, among them iodine, bromine, phosphorus, sulphur, perchromic acid, lithium chloride, fats and resins, salicylic, benzoic and other acids, chloral hydrate, glucosides and alkaloids. Some of them may be recognized by the characteristic color of the solution. Occasionally, ether is added to prevent the solution of portions of the precipitates in the mixture in which they are produced, e. g., ammonium platinic chloride. Mixed with absolute alcohol it serves to extract and separate lithium from other alkaline chlorides. Mixed with alcohol and ammonia it forms Prollius' mixture for alkaloid assays.

TESTS. For most analytical purposes the *stronger ether U. S. P.* is sufficient, but some require *pure absolute ether*. This is a colorless, volatile liquid, neutral to testpapers; does not change the color of white anhydrous cupric sulphate to blue; does not reduce a cooled mixture of sulphuric acid and solution of potassium dichromate to green chromic alum in the cold. It does not dissolve aniline violet; hence, a color communicated indicates alcohol. If entirely free from water, the admixture of an equal volume of carbon disulphide does not render it turbid. It boils at 34.97° C.; its spec. gr. at 17.5° C. is 0.7185.

Pure officinal ether (æther fortior, U. S. P.) has spec. gr. 0.725 at 15°C. It contains 94% of absolute ether, the remainder being alcohol and some water. It boils at 37° C.; hence, the average heat of the human body (37° C.) suffices to boil it, when held in the hand in a test-tube in which a few fragments of glass have been added to the ether.

When 10 Cc. of this ether are shaken with 10 Cc. of glycerin in a graduated cylinder the ethereal layer must, after the separation, occupy no less a volume than 8.6 Cc. Like the absolute, it must be strictly neutral to testpapers.

Ether is sometimes adulterated with benzin (petroleum ether). To detect its presence 5Cc. ether are mixed in a graduated cylinder with 10Cc. conc. sulphuric acid. If pure, the ether will form with the acid a clear uniform liquid; if benzin be present it will float on top,

and may be measured and, after separation, identified by dropping into it a crystal of iodine, which, in benzin, dissolves with violet color; in ether, with brown.

When solution of potassium iodide is added to pure ether no iodine is liberated (absence of hydrogen dioxide or ozone); potassium hydrate must not produce a yellow or brown color (abs. of aldehyde).

PREPARATION. A mixture of five parts of pure, strong alcohol with nine parts of concentrated sulphuric acid is kept in a leaden (or glass) still at a temperature between 130° and 145° C., alcohol being from time to time added, so as to keep a constant volume of the liquid within the still. If the limits of temperature are strictly maintained only ether and water distill over; at lower temperature, alcohol; at higher, sulphur dioxide and ethylene are carried into the condenser. The product separates into two layers; the upper, containing ether, with some alcohol and water, is removed, agitated with calcium hydrate and rectified by repeated distillation, the fractions containing most alcohol and water being separated.

For obtaining *absolute ether* the alcohol is removed by repeated washing with water, and the water by digesting with anhydrous calcium chloride and freshly burnt lime and finally redistilling.

Prollius' mixture is made by mixing 70 Cc. alcohol of 94% with 30 Cc. of ammonia water of 28%, and enough of stronger ether to make 1 litre. A modification of this adds from 250 to 300 Cc. chloroform and lessens the ether by an equal volume.

Ethyl Orange, see *Color Reagents*, page 80.
Eupittonic Acid, see *Color Reagents*, page 80.
Fehling's solution, see *Cupric Tartrate*.
Fernambuco wood, same as *Pernambuco*, see *Brazilwood*, page 58.
Flavescin, see *Color Reagents*, page 80.
Fluorescein, see *Color Reagents*, page 80.
Fluorspar, see *Calcium Fluoride*, page 64.

FLUXES.

These are agents used in the dry (docimastic) assay, which are added to the ores for various purposes. Some act as solvents of the impurities (gangue) accompanying the metals, converting them into fusible slag, such as powdered glass, quartz, kaolin, borax, microcosmic salt, or sodium, potassium and calcium carbonate, fluorspar, kryolite, litharge, etc. Others serve to reduce oxides,

such as charcoal mixed with alkaline carbonates, black flux, potassium cyanide, etc. Others are used to oxidize, as saltpetre and litharge; some of them also decompose sulphides and separate the metal; some serve to concentrate the metal or extract it from the ore by alloying with it, as metallic lead, etc., or to volatilize, as ammonium salts. Others form a cover over the fused ore to exclude air, as sodium chloride, glass, etc.

Most of these reagents are described under their respective headings in other portions of this work, while a few special mixtures find their place here.

BLACK FLUX is a mixture resulting from the deflagration of crude cream of tartar (argols) with a portion of saltpetre not quite sufficient to oxidize all of its carbon. It is used as a reducing agent in the assay of ores of lead, copper, tin, bismuth, nickel, zinc, etc. It is prepared by deflagrating in a red hot crucible, placed under a well drawing flue to carry off the gases, a mixture of saltpetre and argols varying in proportion. For very active reduction three parts of cream of tartar are mixed with one part of nitre. When less active reduction is desired, only 2.5 or even 2 parts of cream of tartar are used. The mixture, before deflagration, is called *raw flux.*

As a substitute for black flux some use a mixture of one part of starch or wheat flour, with from 2 to 5 parts of potassium or sodium carbonate, according to the more or less active reducing properties required.

GRAY FLUX. Is made like black flux from a mixture containing 2 parts of nitre to 3 of cream of tartar. Its reducing property is much smaller than that of black flux.

WHITE FLUX. In this the amount of saltpetre used is from 1 to 2 parts to 1 part of cream of tartar, so that no more unoxidized carbon remains or even some undecomposed nitrate remains to act as an oxidizer. It is prepared like the preceding.

GLASS. Finely powdered crown-glass, free from lead and arsenic, is used either to form a protective cover, or as a solvent of basic ingredients of the ores. Its fusing point should be between those of borax and of fluorspar at about 1200° C. As it acts by the union of its silicic acid with the bases of the ore, it should not contain less than from 60 to 70% of $Si\,O_2$.

In its stead powdered quartz or silicic acid (see on page 19) is sometimes used.

For other fluxes see the articles *Calcium Fluoride*, *Carbonate* and *Sulphate*, *Kaolin*, *Kryolite*, *Potassium Carbonate*, etc., etc.

Froehde's Reagent, see *Sulpho-molybdic Acid,* page 12.
Fuchsine, see *Color Reagents*, page 80.

FUMING SULPHURIC ACID.

Nordhausen Sulphuric Acid.

USES. This acid consists of a combination of sulphur trioxide, SO_3, with sulphuric acid, H_2SO_4. When these are in exact molecular proportion *pyrosulphuric acid* (disulphuric), $H_2S_2O_7$ results; when more SO_3 is present, it fumes in contact with moist air, and is called fuming sulphuric acid.

It is used for dissolving indigo and for preparing organic sulphonic acids; also for the solution of nitrogenous organic bodies and the conversion of their nitrogen into ammonia salt, according to *Kjeldahl's* method; also in gas analysis for the absorption of heavy hydrocarbon gases.

TESTS. In most cases the commercial acid is sufficiently pure. If desirable to test it qualitatively, the same method is employed as with ordinary sulphuric acid (page 22), great caution being necessary in diluting the acid. For quantitative analysis of its sulphur trioxide the volumetric method may be used; the specimen is weighed in a very small flask, this is carefully set up into a beaker, whose bottom is covered with water, insufficient to reach the neck of the little flask; the beaker is covered and left to stand for several days, so that the acid in the flask may first very gradually dilute itself, by attracting moisture, before an attempt is made to mix it with more water for proper dilution.

PREPARATION. On the large scale, fuming sulphuric acid and sulphur trioxide are made by the dry distillation of ferrous sulphate or acid sodium sulphate. On the small scale, it may be made by mixing pure concentrated sulphuric acid with sulphur trioxide (now easily obtainable in the market), or by adding to it phosphorus pentoxide sufficient for dehydration. See *Sulphur Trioxide.*

Furfurol, $C_5H_4O_2$ (pyromucic aldehyde), is occasionally used to detect urea, which is colored violet by addition of a saturated aqueous solution of furfurol, followed by hydrochloric acid. It is obtained as a bye-product of the manufacture of garancin from madder; also by distilling one part of wheat or rye bran with one part of conc. sulphuric acid and three parts of water, and rectifying the distillate over sodium carbonate and chloride.

GALLS.

A 10% infusion of galls in water or dilute alcohol contains both tannic and gallic acid, and is sometimes used to detect iron, with

which it produces a greenish-blue to black color, according to the state of oxidation, and finally a black precipitate. It also serves as a precipitant of gelatin. When a small amount of iodine solution is added it indicates alkalies by an evanescent rose-red color. It is now seldom used, pure tannic or gallic acid being preferred.

GELATIN.

USES. For removing tannic acid from vegetable extracts (detannation). Also in standardized solution for volumetric determination of tannin. The aqueous extract containing the tannin is mixed with an equal volume of a saturated solution of ammonium chloride, and the standardized solution of gelatin added till no more precipitate falls. The observation of this endpoint is facilitated by the presence of ammonium chloride and chromic alum, which cause the flocculent precipitate to separate rapidly and leave a clear solution. Dry gelatin also serves to collect alum from infusions of bread or flour adulterated with it.

PREPARATION. Ten parts of isinglass, or other pure variety of gelatin, are dissolved by the aid of heat in water, saturated in the cold with ammonium chloride, and containing 0.5 gr. of chromic alum. After the gelatin solution has cooled, enough of the ammonium chloride is added to make 1 litre. The titre is adjusted to correspond to pure tannic acid.

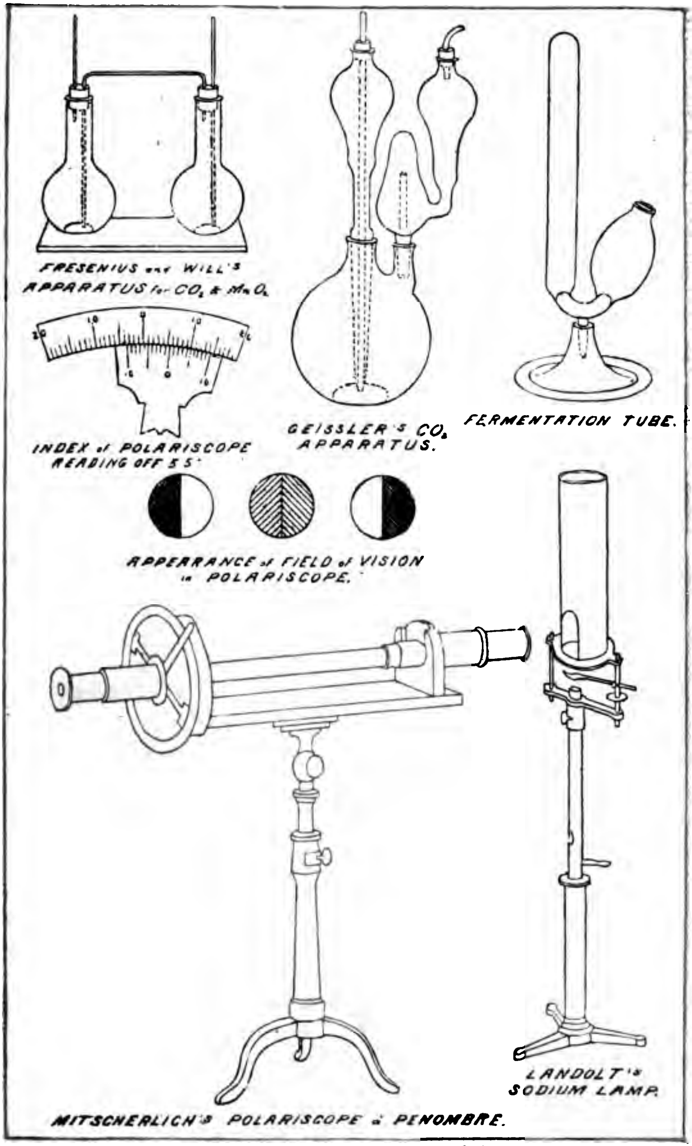
GLUCOSE, $C_6H_{12}O_6$.

Dextro-glucose or Grape Sugar.

USES. To adjust the titre of Fehling's solution and as a reducent.

TESTS. By the polariscope. A solution containing in 100 Cc. 10 gr. of anhydrous glucose, at 20° C. in a tube 200 Mm. long, turns the plane of polarization 10.6°, sodium light being used as illuminator. In an instrument graduated to read per cent of glucose, the percentage of the solution must accurately coincide with the reading.

PREPARATION. Mix 2,500 Cc. of 90% alcohol with 100 Cc. of most concentrated hydrochloric acid, keep the temperature at 45° C. and dissolve in it 800 gr. of pure cane sugar. In about two hours the inversion into dextrose and lævulose is complete. Set aside in a cool place for several days. The dextrose (glucose) will then separate in crystals, while acid and lævulose remain in solution. The crystals are drained on a glass funnel, washed with alcohol until all acid has been removed; then they are dissolved in hot alcohol (methyl alcohol is preferable) and recrystallized. The recrystallization is repeated once or twice, the product is then powdered and dried sharply at 102°C. Pure anhydrous glucose is the result.



Charlotte S. Cushman Del.

Glycerin, see *Alcohols*, page 28. For absolutely pure glycerin the following tests are added: After evaporation, at moderate heat, upon a slip of glass the microscope must show by transmitted light neither turbidity nor black or brown coloring of the spot occupied by the glycerin. A mixture of 2 Cc. each of glycerin and ammonia water (10%), heated to boiling in a test tube, must, after addition of 0.5 Cc. solution of silver nitrate, remain clear and colorless for at least 5 minutes.

GOLD, Au.

USES. Metallic gold is used for the preparation of gold chloride (aurochloric acid). Also in the docimastic assay, by Plattner's method, of nickel ores or alloys, containing a small percentage of copper, for the purpose of preventing the slagging of the copper while nickel and arsenic, etc., are removed by oxidation. In thin foil it sometimes serves instead of copper for the recognition of mercury.

TESTS. Are made with its solution and are the same as those for gold chloride, as described in the next article.

PREPARATION. Coin gold is dissolved in a minimum of cold nitrohydrochloric acid (see page 15). The solution is set aside for several days to deposit all of its silver chloride. It is then decanted and precipitated with pure ferrous sulphate, dissolved immediately before use in boiled distilled water. The fine gold powder is permitted to settle in a warm place, the liquid is then poured off and the sediment repeatedly washed. It may then be used directly for preparation of gold chloride or fused with pure potassium nitrate and borax.

AURIC CHLORIDE, $Au\,Cl_3 + 2\,H_2O$; AURO-CHLORIC ACID. $Au\,Cl_3 . H\,Cl + 4\,H_2\,O$.

Gold Chloride.

USES. Aurochloric acid is used to detect tin by the precipitation of the purple of Cassius. The more neutral auric chloride is employed in the analysis of alkaloids, many of which it precipitates from solution, forming with them double salts. In a solution of albumin acidulated with formic acid the addition, drop by drop, of a 1% solution of gold chloride and heating, produces, first, a rose-red, then a purple color, changing, on further addition of gold solution, to blue.

TESTS. A dilute solution, heated gently with some excess of oxalic acid, must, after separating the metallic gold by filtration, leave no permanent residue on evaporation. Addition to a concentrated solution of ammonium or potassium chloride must produce no precipitate.

PREPARATION. Aurochloric acid is made from the pure gold, obtained by precipitation by ferrous sulphate or oxalic acid and thorough washing. It is dissolved in a minimum of pure nitro-hydrochloric acid (see page 15), and, after solution, concentrated on a water bath, while a small amount of hydrochloric acid is added. The residue, on cooling, forms yellow crystals of $Au\,Cl_3 . H\,Cl + 4\,H_2\,O$, which are dissolved in 30 parts of water. If the gold chloride, $Au\,Cl_3$, is to be made, the addition of H Cl is omitted and the evaporation conducted at a somewhat higher temperature (110° C.). The dry residue is either dissolved for use in 30 parts of water or crystallized by addition of water and evaporation at 100° C. A temperature of 185° C. completely decomposes auric chloride into aurous chloride and free chlorine.

Guaiacum, see *Color Reagents*, page 81.

Gurjun, see *Dipterocarpus Oil*, page 101.

Hæmatoxylin, see *Logwood* in *Color Reagents*, page 84.

Hydriodic Acid, see on page 7.

Hydrobromic Acid, see on page 7.

Hydrocœrolignone, $C_{16}\,H_{18}\,O_6$, is recommended by *Liebermann* as a most delicate reagent for quinone. Even in very dilute aqueous solutions of quinone the addition of a few drops of alcoholic solution of hydrocœrolignone produces at first an orange color, then a steel-blue precipitate of cœrolignone.

It may be prepared from cœrolignone by reduction with nascent hydrogen (boiling with zinc and hydrochloric acid). Cœrolignone separates when crude pyroligneous acid is mixed with potassium dichromate as a steel-blue precipitate, which is purified by dissolving in phenol and precipitating by alcohol.

Hydrochloric Acid, see on page 8.

Hydrofluoric Acid, see on page 9.

Hydrofluosilicic Acid, see on page 10.

HYDROGEN, H.

USES. For the preparation of pure metals by reducing metallic oxides. In the determination of copper as cuprous sulphide. In gas analysis for determination of oxygen by explosion. For the production of high temperatures by burning with oxygen in the compound blowpipe in the assay of refractory metals.

TESTS. Pure hydrogen, when burnt from a jet, does not produce any spots on a cold piece of porcelain held into the flame. The water condensed on the porcelain must have a perfectly neutral reaction; the products of the combustion passed into lime or baryta water must not render it turbid. A paper moistened with silver nitrate must not be blackened by the gas.

PREPARATION. In small quantities, for gas analysis, pure hydrogen gas may be made by the electrolysis of very dilute, pure sulphuric acid. Also by heating palladium which had previously been saturated with hydrogen at 100°; or by bringing pure zinc and pure acid together in one of the compartments of a gasburette. On a somewhat larger scale, for reductions, pure, dry hydrogen gas is made by placing pure zinc and pure dilute sulphuric acid into a suitable gas generator, connected with a series of tubes or flasks for purification; first, a simple wash flask to retain any particles of acid carried over mechanically; then one filled with solution of potassium permanganate, next with sodium hydrate, and lastly, with anhydrous calcium chloride, to remove moisture. For use in the compound blowpipe, the presence of carbon in zinc, otherwise pure, does not interfere.

HYDROGEN DIOXIDE, H_2O_2.

USES. To oxidize, in alkaline solutions, the sulphur of metallic sulphides, sulphuretted hydrogen, or polythionates to sulphuric acid, which may then be determined as barium sulphate (*Classen and Bauer*) or volumetrically (*Eliasberg*), thereby also allowing the determination of chlorides, bromides and iodides, when H_2S is present. Also to detect titanic, molybdic and vanadic acid by coloration of yellow to orange-red (Schoenn). Also in the analysis of nitro-glycerin and other nitro-compounds by oxidizing N_2O_3 to N_2O_5 (*Hampe*). For recognition of chromic acid and chromates by their conversion into a deep blue substance, whose composition is as yet unknown (usually called perchromic acid), soluble in ether.

TESTS. A solution of hydrogen dioxide is so liable to deterioration by decomposition into water and oxygen gas that an estimation of its strength should be made by the depth of the blue color produced with potassium and dichromate solution. A small percentage of free acid preserves it longer, but care should be taken that another acid should be used than that which is to be determined. Hence, for determining sulphides it must not contain sulphuric acid, nor hydrochloric, if chlorides are to be detected. For oxidizing the lower oxides of nitrogen, phosphoric acid might be added. The solution should leave no permanent residue on evaporation.

PREPARATION. Pure barium dioxide, suspended in water, is very gradually added to an ice cold mixture of 1 part of pure sulphuric acid with 5 parts of water, the vessel being surrounded by ice and the mixture being constantly stirred until the acid is nearly neutralized. After filtration, the excess of acid is carefully removed by the addition of baryta water. The liquid is filtered again and

preserved in a cool dark place. It may be concentrated by freezing the water and decanting the concentrated solution.

Hydrogen Sulphide, see *Hydrosulphuric Acid,* page 10; also *Barium Sulphide,* page 52. To free hydrogen sulphide from *arsenic,* hydrochloric acid in various states of dilution is used in a system of four wash bottles, the contents of which are kept at 60° to 70° C. The first has 1 part of hydrochloric acid with 2 parts of water; the second, 1:4; the third, 1:8; the fourth, distilled water. No rubber is used about the apparatus (*Lenz*).

HYDROXYLAMINE HYDROCHLORATE, $NH_2OH.HCl$.

USES. For quantitative determination of silver, which is reduced to metal by hydroxylamine hydrochlorate and potassium hydrate from its haloid salts and their solutions in sodium hyposulphite (*Lainer*). Also to recognize aldehydes and ketones by converting them into isonitroso compounds (acetoximes), in which the group $= C = O$ is replaced by $= C = N - O - H$ (Nægeli, V. Meyer).

TESTS. Hydroxylamine hydrochlorate forms transparent monoclinic crystals, soluble in water and in alcohol. Absence of ammonium chloride must be shown by platinic chloride producing no turbidity in its solution. The salt melts at 151° C., and, on further heating, suddenly decomposes, leaving no permanent residue.

PREPARATION. Pure nitromethan, $CH_3 . NO_2$ is prepared from silver nitrate and methyl iodide. This is mixed with dilute hydrochloric acid in molecular proportion, and placed in stout glass tubes, sealed hermetically. These are placed into a suitable safety envelope and heated not to exceed 150° C. A solution of hydroxylamine salt and CO are formed. After opening the tubes the solution is carefully concentrated by evaporation, the crystals are redissolved in hot absolute alcohol, and on its evaporation are carefully preserved in opaque vessels.

Indigo, see *Color Reagents,* page 82.

Indol, C_8H_7N, is occasionally used to detect, under the microscope, lignin in vegetable tissues, in paper, etc., by coloring it intensely red. It is, however, much inferior to aniline sulphate for this purpose.

IODINE, I.

USES. In connection with potassium hydrate to detect, by the formation of iodoform ethyl, propyl, butyl and capryl alcohols, acetic, propionic and butyric aldehydes, quinic, meconic and lactic acids, methyl butyrate, methyl benzoyl and oil of turpentine (*Lieben*). To detect metallic mercury in sublimates in glass tube

by conversion into $Hg\ I_2$. To detect bismuth by the blow-pipe test as scarlet oxyiodide. To detect tannic, gallic and pyrogallic acids by an evanescent purple-red color (*Nasse*). In gas analysis it is used to absorb carbon disulphide (*Eiloart*). To identify starch by its blue-black coloration, especially starch granules in situ under the microscope, iodine is used either as iodine-water, a saturated solution of iodine in distilled water containing about 0.014% of iodine, or as a solution in dilute alcohol, glycerin or potassium iodide solution. A solution of iodine in zinc chloride, or of iodine in water, followed by concentrated sulphuric acid, colors cellulose blue. In volumetric analysis a solution of iodine and potassium iodide (mostly of decinormal strength) is used with a companion solution of sodium hyposulphite (thio-sulphate) and starch solution as indicator for a great variety of determinations. It permits the estimation of arsenic trioxide and arsenites, chlorine and hypochlorites, sulphites, hyposulphites, chromates, chlorates, manganese dioxide, etc. Also of acetone by the formation of iodoform and measuring back the surplus of iodine, and of many other substances by either direct or indirect methods. It is also used to precipitate many alkaloids, forming with some of them characteristic compounds. An alcoholic solution of iodine is sometimes used to add to oils, with which some of the iodine unites, enabling a differentiation of the oils by measuring volumetrically the amount of iodine retained, which is expressed in per cents of the oil, and called the iodine-addition number (*Hubl*). Atom. W. $I = 126.559$.

TESTS. When heated in a test-tube pure iodine completely volatilizes, showing no deposit of moisture at first, nor colorless crystals in its sublimate, nor leaving a trace of residue. Its solution in chloroform must be perfectly clear. To distilled water, recently boiled to expel absorbed gases, it should impart only a light brown color (a deeper brown indicating presence of hydriodic acid, chloride of iodine, etc.). To detect iodine cyanide, water saturated with iodine is shaken with pure carbon disulphide until all color of iodine is removed, and, after settling of the iodine solution in $C\ S_2$, a portion of the clear liquid is carefully decanted. In this a small granule of ferrous sulphate is dissolved, then a few drops of ferric chloride are added, and lastly some potassium hydrate. After digesting the mixture for some time it is acidulated with hydrochloric acid. A blue precipitate of ferric ferrocyanide would indicate presence of iodine cyanide. After converting the iodine into silver iodide, ammonia water must not dissolve any portion of it. Hence, after filtration and acidulating with nitric acid, it must remain

clear. Perfectly pure resublimed iodine is now easily obtainable from dealers.

PREPARATION. Commercial iodine is powdered and heated to 100° C. on a water-bath in a porcelain dish for about 15 to 20 minutes. The vapor is either suffered to escape or condensed upon the bottom of a flask filled with cold water. This removes any iodide of cyanogen, which volatilizes at 45° C. and forms colorless crystals, adhering to the cold flask. All moisture is also driven off and chloride of iodine mostly decomposed or volatilized. After 20 minutes the remaining iodine is thoroughly mixed with about five per cent of pure dry potassium iodide to decompose any remaining chloride or bromide of iodine. It is then returned to the porcelain capsule, which is closely covered with a clean glass funnel, and slowly heated on a sand-bath so as to sublime the iodine, which adheres in large crystals to the funnel. It must be carefully preserved in close vessels.

Deci-normal solution is made by adding 12.66 gr. of pure iodine to a solution of 18 grammes of pure potassium iodide in 900 Cc. water, dissolving by agitation, avoiding heat and filling up to 1 litre.

See also *Sodium Hyposulphite* and *Starch*.

IRIDIUM-SODIUM CHLORIDE, $Ir\,Cl_4 . 2\,Na\,Cl + 6\,H_2O$.

USES. The aqueous solution of the black crystals of this salt has been used in the analysis of alkaloids, some of which it precipitates, while morphia is not precipitated by it (*Planta*).

As pure metallic iridium only dissolves when in the state of minutest subdivision, but is easily dissolved as alloyed with platinum and other metals, it is not advantageous to prepare its salts on the small scale; they are obtained as bye-products at the platinum-affineries and sold by dealers in a sufficiently pure state.

IRON AND ITS COMPOUNDS.

IRON, Fe.

USES. In the metallic state iron is used to detect copper by reducing it from its salts, showing a red film of metallic copper upon the iron. For this purpose any bright piece of sheet iron or wire is suitable. Minute traces of copper are detected by using a bright steel needle as electrode of a battery. In the wet assay copper is completely precipitated by pieces of iron wire placed into the acidulated solution. It is also used for the preparation of salts, for adjusting the titre of volumetric solutions of potassium dichromate or permanganate. For this purpose the fine, soft wire

used by florists is sufficiently pure, when bright and free from rust. $Fe = 55.913$.

TESTS. The gas evolved from absolutely pure iron and pure dilute hydrochloric or sulphuric acid must be inodorous and not blacken a drop of silver nitrate placed on filter paper over the test-tube from which the gas is evolved. The solution resulting must be clear and without flocculi, nor must any part of the iron remain undissolved. It must not yield a precipitate with hydrogen sulphide. After precipitation of the solution, neutralized with ammonia, by ammonium sulphide, the filtrate must leave no residue after evaporation and ignition.

FERRIC ACETATE, $Fe_2(C_2H_3O_2)6$.

USES. When perfectly neutral ferric acetate in very dilute solution is mixed with potassium sulphocyanate, no reddening occurs from the formation of ferric sulphocyanate until free acid is added. Hence, the mixed solutions are employed to detect free acid (*Mohr*). Presence of sodium acetate interferes with the reaction. Ferric acetate is also used in the analysis of tannins, in the place of skin powder, to precipitate tannic acid.

TESTS. The solution must not contain free acid. When diluted so as to show only a faint yellow color, a few drops of potassium sulphocyanate solution must not produce a red color, until a drop of hydrochloric acid is added. The U. S. P. preparation is too acid to be used for this test.

PREPARATION. 5.5 gr. of ferric chloride are dissolved in water and poured into ammonia water in slight excess, so as to precipitate the ferric hydrate completely. The precipitate is thoroughly washed and dissolved in 3.5 grammes of glacial acetic acid without the aid of heat. The small residue left undissolved is filtered off and the solution diluted to 100 Cc. It should be carefully preserved in a cool, dark closet.

FERRIC CHLORIDE, $Fe_2Cl_6 + 12\ H_2O$.

USES. As a group reagent for organic acids not precipitated by calcium chloride. It produces with succinates and benzoates brownish, with ferrocyanides blue, with tannates blue-black precipitates; acetates, formates, sulphocyanates, pyrogallates and meconates are colored red, ferricyanides brown, gallates black, salicylates violet. Of organic bases it colors aniline red, morphine blue, while codeine, thebaine, papaverine and narcotine are left colorless, and narceine colored blue only after partial decomposition by heat. Thalline, even in minute traces, is colored

green by ferric chloride, antipyrine brown-red, etc.; phenol is colored violet, and, in aqueous solution, all phenols, aromatic oxy-acids, carbohydrates and alcohols give characteristic color reactions with very dilute ferric chloride, so that *Landwehr* proposes it as a general reagent for the presence of the hydroxyl group. In conjunction with ammonia very dilute solutions of ferric chloride color many organic sulph-hydrates a deep red-brown (*Claesson*). It is also used to decompose phosphates of alkaline earths, and to remove their phosphoric acid. In conjunction with potassium nitrite it serves to detect small quantities of hydrocyanic acid by converting it into nitroprusside, which is readily known by its reaction with alkaline sulphides (*Vortmann*). Mol. W. $Fe_2 Cl_6 = 324.046$.

TESTS. Ferric chloride must dissolve without residue in water or alcohol; it must be free from ferrous salt; hence, it must give with freshly prepared potassium ferricyanide solution a clear brown color, without shade of green or trace of precipitate. It must be perfectly neutral, so that when stirred with a glass rod dipped into ammonia water a permanent brown-red precipitate is formed. Absence of the nitrogen acids must be shown either by ferrous sulphate and sulphuric acid, or after precipitation of the iron by ammonia, in the filtrate, by diphenylamine or pyrogallol and sulphuric acid. Absence of sulphates is shown by barium chloride. After precipitation of the iron by ammonia the colorless filtrate must not yield a precipitate with ammonium sulphide, nor leave, on evaporation, a permanent residue. After addition of an excess of ammonium acetate and boiling until the iron is completely precipitated as basic acetate, the filtrate must leave after evaporation, no fixed residue. After acidulation with hydrochloric acid sulphuretted hydrogen must produce a pure white precipitate of sulphur, which volatilizes without residue.

PREPARATION. Ferrous chloride is first made by gently heating in a large flask 1 part of pure, fine iron wire with 4 parts of hydrochloric acid, of spec. gr. 1.16, until no more hydrogen gas is evolved. The solution is separated from the small excess of iron, and converted into ferric chloride by passing into it pure chlorine gas (the absorption being hastened by frequent agitation) until a drop taken out gives a pure brown color to a fresh solution of potassium ferricyanide. The excess of chlorine is now expelled by moderate heat and the solution placed under the bell glass of an exsiccator to crystallize. If wanted in solution it is diluted so that for 1 gr. of iron used 20 Cc. are obtained. The process of preparation by the aid of nitric acid, as usually employed, yields a product from which the last traces of the oxides of nitrogen are difficult to remove.

FERROUS CHLORIDE, $Fe\,Cl_2$.

Uses. Ferrous chloride, dissolved in strong hydrochloric acid, is used for the quantitative determination of nitric acid and nitrates, according to *Schloesing's* and other modified methods. Also for converting arsenic into the volatile $As\,Cl_3$, which is separated by distillation and its quantity ascertained (*Beckurts*). Occasionally, it serves in the separation of selenium. Mol. W. = 126.653.

Preparation. Ferrous chloride is only prepared when required for instant use, as it can be preserved only with difficulty. Pure, fine iron wire is then dissolved in pure hydrochloric acid of such concentration as is suitable for the special work; the vessels in which the solution is made are filled either with hydrogen or carbonic acid gas to prevent decomposition by atmospheric oxygen.

Ferric dinitrosulphide is made, according to *Hoffmann and Power*, by adding a solution of ferric chloride or sulphate, drop by drop to a mixture of equal parts of concentrated solutions of potassium nitrate and ammonium sulphide. The mixture is boiled for a few minutes, filtered while hot from the sulphur, and set aside to deposit, on cooling, black, rhombic crystals of ferric dinitrosulphide. These are dissolved in 10 parts of water.

Ferric Ferricyanide is made only when needed by mixing the freshly prepared solution of potassium ferricyanide with ferric chloride. The brown solution is reduced more or less rapidly by morphine and many other alkaloids and by most ptomaines, so that a deep blue precipitate of ferric ferrocyanide (Prussian blue) or of ferrous ferricyanide (Turnbull's blue) is formed.

Ferric Oxide, $Fe_2\,O_3$, is used in the docimastic assay of copper. The commercial article is sufficiently pure.

Ferric Sulphate, $Fe_2\,(S\,O_4)_3$, and *ferric ammonium sulphate*, $Fe_2\,(S\,O_4)_3\,.\,(N\,H_4)_2\,S\,O_4 + 24\,H_2\,O$ (ferric alum), are sometimes used in 10% solution as indicators in the titration of silver by ammonium rhodanate. Freedom from chlorine is the only requisite of purity.

FERROUS SULPHATE, $Fe\,S\,O_4 + 7\,H_2\,O$.

Uses. The tendency of ferrous sulphate to change to ferric salt makes it a powerful reducent. As such it serves to precipitate gold; to recognize nitric acid by reducing it to N O, which dissolves in the remaining solution of ferrous sulphate with a dark-brown color. By heating this brown color disappears readily. A similar reaction is produced by acids of selenium, but then, heating does not cause the brown color to disappear, but rather to become more intense, and finally change to a red precipitate of se-

lenium. It is also used to detect ferricyanides by forming with them Turnbull's blue; also tannic acid, with which, when perfectly free from ferric salt, it gives a white gelatinous precipitate, turning blue-black in air, while with gallic acid no precipitate is formed, but the colorless solution turns blue in air. Mol. W. = 277.457.

TESTS. The pale bluish-green, monoclinic crystals must be free from yellow spots of ferric salt and form with water a perfectly clear pale greenish solution, whose reaction is neutral or but feebly acid. After acidulation with a drop of hydrochloric acid this solution must yield no precipitate with hydrogen sulphide. If, after being acidulated by boiling with sufficient nitric acid, the solution is precipitated by excess of ammonia water and the ferric hydrate filtered off, the filtrate, divided into three portions, must give no precipitate with ammonium sulphide (abs. of zinc), nor have a blue color or after acidulation by acetic acid give a red-brown precipitate with potassium ferrocyanide (abs. of copper) nor after evaporation and ignition leave any residue.

PREPARATION. An excess of clean, fine iron wire is dissolved in pure, dilute sulphuric acid, the solution filtered, acidulated slightly with sulphuric acid and concentrated. The crystals are drained on a funnel washed with a little acidulated water, dried and carefully preserved. The solution is only made when needed, with water previously boiled to expel oxygen.

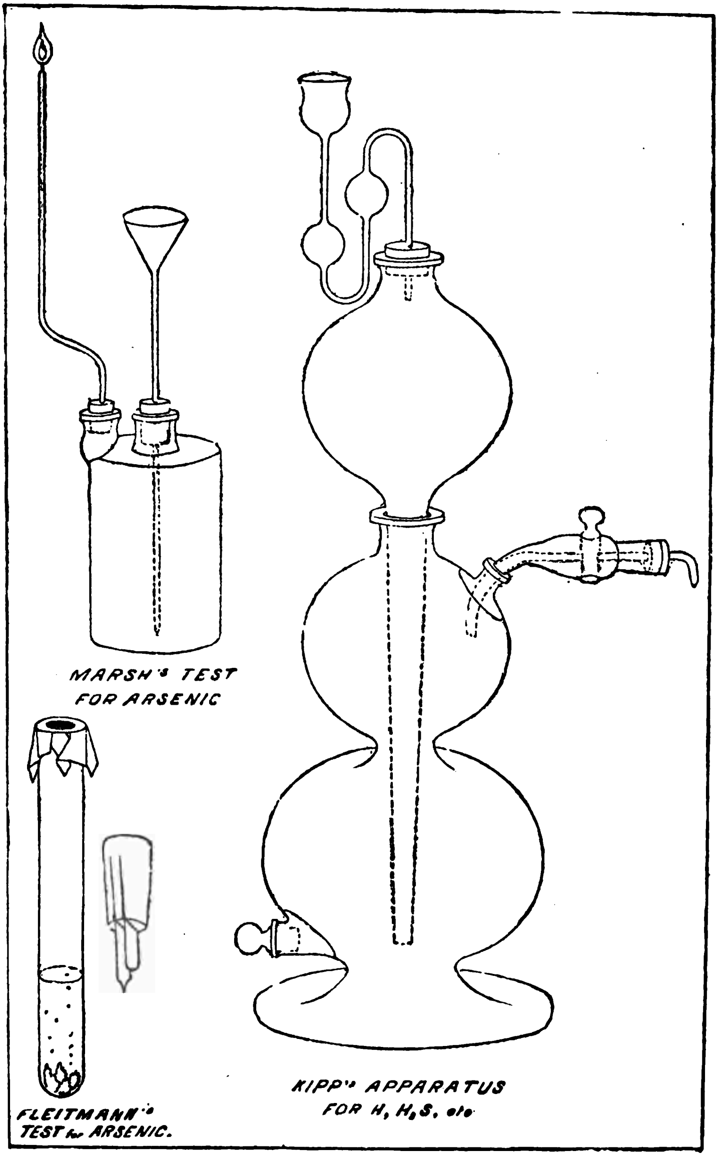
A very good article may be obtained from the residue of the sulphuretted hydrogen apparatus, if pure ferrous sulphide and pure acid have been employed.

FERROUS AMMONIUM SULPHATE, $Fe\,S\,O_4\,(N\,H_4)_2\,S\,O_4 + 6\,H_2O$.

USES. This salt serves for the same purposes as ferrous sulphate; being less liable to oxidation it is also used in volumetric analysis for adjusting the titre of potassium permanganate solution. Mol. W. = 391.363.

TESTS. This salt must, in addition to the same tests as ferrous sulphate, stand a quantitative comparison with pure iron, so as to show that it reduces an equivalent amount of potassium permanganate. 3.91363 gr. must require the same number of Cc. of permanganate, as 0.55913 gr. of iron.

PREPARATION. 277.457 gr. of pure crystals of ferrous sulphate and 131.866 gr. of pure ammonium sulphate are separately dissolved in a minimum of water at 70° C., mixed, a few drops of sulphuric acid added, and permitted to cool while constantly agitated, so as to form very small crystals. These are carefully dried and preserved.


MARSH'S TEST
FOR ARSENIC
FLEITMANN'S
TEST for ARSENIC.
KIPP'S APPARATUS
FOR H, H_2S, etc.

FERROUS SULPHIDE, $Fe\,S$.

USES. For the preparation of hydrogen sulphide.

TESTS. For most purposes the commercial ferrous sulphide furnishes gas of sufficient purity, especially if care is taken to thoroughly wash it. But as arsenic and phosphorous are rarely entirely absent, even in the purer article furnished by the trade, an absolutely pure article must be made from pure iron and pure sulphur for accurate work, especially in forensic cases. *Van der Pfordten* states that passing the gas over fusing potassing sulphide at 350° C. furnishes hydrogen sulphide free from arsenic, even though very crude ferrous sulphide be used. Arsenic may be detected by dissolving the finely powdered ferrous sulphide in nitromuriatic acid, removing the excess of nitric acid by evaporation, and adding to the residue zinc and hydrochloric acid in a test tube covered with a cap of filter paper, on which a drop of concentrated silver nitrate solution will indicate the presence of arsenic by turning first yellow and, on moistening, black (*Gutzeit's test*).

PREPARATION. Pure, fine iron wire, cut in pieces of suitable length, is heated to bright redness in a hessian crucible, pieces of pure sulphur are then gradually added until the mass is well-fused; any excess of sulphur volatilizes. The fused mass is poured on a clean place, so as to form thin plates, which are broken into pieces of suitable size.

Ferrous sulphide remaining after having been immersed in the acid of the apparatus, although well washed, rapidly deteriorates by oxidation, unless it be covered by glycerin. (*Kubel.*)

FERROUS POTASSIUM OXALATE, $Fe\,K_2\,(C_2\,O_4)_2 + 2\,H_2\,O$.

USES. This reagent has been introduced by *Eder* as a general reducent of metals from their salts. It reduces at ordinary temperatures platinic chloride, potassium-platinic chloride, silver nitrate, chloride, bromide and iodide to the metallic state; from mercuric chloride it precipitates metallic mercury by heating; ferro- and ferri-cyanides of iron are converted into the yellow potassium ferrocyanide, etc. The reagent acts not only in alkaline and in neutral, but also in acid solutions. Mol. W. =345.447.

PREPARATION. To concentrated solution of pure ferrous sulphate a concentrated solution of pure potassium oxalate is added, with constant stirring, until the precipitate of ferrous oxalate at first formed is redissolved, forming a clear, deep-red solution. Or else dry ferrous oxalate is boiled with a 30% solution of potassium oxalate until no more is dissolved. The dry double salt is very unstable, it decomposes with water, and remains in solution only through excess of potassium oxalate.

Isinglass, see *Gelatin*, p. 106.

KAOLIN.

This native silicate of aluminium is used occasionally as a flux in dry assaying; also in the state of powder as an inert addition to vegetable powders to prevent them from adhering together while being extracted by a solvent. It should be of a pure white color and yield nothing soluble to water or to very dilute hydrochloric acid.

KRYOLITE, $Al_2 F_6 . 6 Na F$.

USES. This native mineral, consisting of aluminium and sodium fluoride, is used in the place of fluorspar for the preparation of hydrofluoric and hydro-fluo-silicic acid; also, in dry assays, as a flux for removing silicic acid.

Only pure white, translucent pieces, free from foreign enclosures must be selected.

LEAD AND ITS COMPOUNDS.

LEAD, Pb.

USES. Metallic lead, either granulated or in foil (for cornets), is used in the docimastic assay of ores and alloys of silver, gold, platinum, etc. For this purpose it must be either absolutely pure or, if containing silver only, this percentage must be accurately known, so as to be deducted in the calculation. The lead, during the process of cupellation, becomes oxidized and then yields its oxygen again to the sulphur, arsenic or antimony combined with the metals and helps, together with the borax used at the same time, to form slag, while the rest of the fused lead dissolves the silver, gold, etc., and after oxidation leaves them behind as a "button." Various amounts of test lead are used according to the quality of the ore or alloy. The weight in these operations is frequently expressed in *assay-tons*. The American assay-ton = 29.166 grammes (450.26 grains troy), so that the number of milligrammes of metal found in 1 assay-ton of ore corresponds to the number of troy ounces in 1 ton of 2,000 pounds avoirdupois. Pb = 206.471.

TESTS. Pure lead has spec. gr. 11.37, and melts at 326° C. When perfectly pure melted lead shows a convex surface like mercury, a flat surface indicates impurities. For most purposes it is sufficient to test 1 assay-ton by cupellation, when it must leave either no residue or one of pure silver, which is weighed and noted for correction. When greater accuracy is required the test lead is dissolved in pure, dilute nitric acid and must stand the following tests: After great dilution a few drops of hydrochloric acid must

either give no precipitate or one which will dissolve readily in ammonia water, indicating silver. A portion of the nitrate solution is then precipitated with pure dilute sulphuric acid, the mixture is evaporated until all the nitric acid is expelled and vapors of sulphuric acid begin to rise The residue, still containing a small excess of sulphuric acid, is mixed with dilute alcohol and filtered. From the filtrate the alcohol is evaporated and the silver (if any) precipitated by hydrochloric acid and filtered off. The clear filtrate on evaporation and ignition must leave no residue; another portion must give no arsenic reaction; another should yield no precipitate with hydrogen sulphide, nor, after addition of ammonia, with ammonium sulphide.

PREPARATION. The purest lead from "Pattinson" process is sufficiently pure for most purposes, and is either rolled into sheet or foil or granulated by agitation while melted. For absolutely pure metal it must be reduced from a pure lead salt by electrolysis. Or the purest litharge obtainable is fused and, from time to time, some lamp black (or oil) is sprinkled upon the surface. This reduces a small portion of the oxide to metal, which dissolves the silver and, by means of its greater specific gravity, sinks to the bottom; from thence it is removed and the operation repeated. Finally, the main bulk of the litharge is reduced and is now free from silver.

LEAD ACETATE, $Pb(C_2H_3O_2)_2 + 3 H_2O$.

USES. For the detection of hydrogen sulphide paper moistened with solution of lead acetate is often used, and shows its presence by the brown to black color of the lead sulphide formed. Also for the detection and precipitation of several acids, some of which are recognized by characteristic color or other properties, among them chromic, hydriodic, phosphoric, malic acid, etc. For the removal from urine of mucin, albumin, etc., by precipitation. For the precipitation of tannic acids and coloring materials, etc., from vegetable extracts. Also for the preparation of basic lead acetate and of pure lead. It is also used for the detection of glucose and lactose. When a solution of lead acetate and then ammonia water, drop by drop, are added to solutions of sugars, urine, etc., the white precipitate indicates the presence of glucose or lactose by assuming a red color after standing for some time (*Rubner*).

It also serves to separate gallic from tannic acid, the lead salt of gallic acid being soluble, that of the tannic insoluble in acetic acid (*Guyard*).

In very dry air or in the exsiccator it loses its water of crystallization and becomes anhydrous. $Pb(C_2H_3O_2)_2 = 324.207$.

TESTS. Pure lead acetate crystallizes in transparent monoclinic tables, soluble without residue in 1.8 parts of pure water, at 15° C., from which carbonic acid has been expelled by boiling. A slight residue of carbonate must dissolve in dilute acetic acid. In alcohol about an equal weight of lead acetate dissolves at 70°C. On cooling, $Pb(C_2H_3O_2)_2 + 2H_2O$ precipitates, leaving less than 4% in solution. With litmus, but not with phenol-phthalein, lead acetate gives an alkaline reaction, Potassium ferrocyanide must produce a pure white precipitate. After precipitation of the aqueous solution by hydrogen sulphide, and the expulsion of the excess of H_2S by boiling, the filtrate must not form a precipitate with silver nitrate, nor with barium chloride, nor yield on evaporation a fixed residue. The watery solution, after precipitation with ammonium carbonate, must show no blue color. The U. S. P. preparation is sufficiently pure for nearly every purpose.

PREPARATION. The test solution is made by dissolving one part of lead acetate in ten parts of pure water.

LEAD SUBACETATE SOLUTION.

Under this general designation a solution of several basic lead acetates, in various proportions, is known. That used in analysis corresponds with the preparation of the Ph. Germ., and contains nearly equal proportions of triplumbic acetate, $2Pb(C_2H_3O_2)_2 + Pb(OH)_2$, and diplumbic acetate, $Pb(C_2H_3O_2)_2 + Pb(OH)_2$, while that made according to the U. S. P. contains principally the latter salt, but may in most cases be substituted for the other.

USES. For the separation of gums, tannic acids, coloring materials, etc., from vegetable extracts, syrups, sugars, beer, urine, etc., previous to examination by the polariscope or by reagents for sugars, alkaloids and other substances not precipitated by the lead salt. Also for the determination of lactic acid (*Palm*). Also for the precipitation of albuminoids, to separate them from peptones, etc., in which case the lead solution is mixed with alcohol. (*Palm*).

TESTS. It should conform to the same tests for freedom from impurities as the neutral acetate, when wanted quite pure. For most purposes the pharmacœpial preparations are sufficiently pure. Spec. gr. 1.228 to 1.24.

PREPARATION. Into a very strong and capacious flask 300 gr. of pure lead acetate, 100 gr. lead monoxide (pure litharge) and 1 litre of water are placed and secured to the flywheel of some moving machinery, so as to keep the mixture thoroughly agitated for from 10 to 12 hours; or heat is applied on a water bath, with occasional

shaking, for a less time. The mixture is then filtered and carefully preserved from contact with carbonic acid.

LEAD CARBONATE, $Pb\,C\,O_3$, and the basic *white lead*, $Pb\,(O\,H)_2 \,.\, 2\,Pb\,C\,O_3$, are used as flux instead of litharge or other lead compounds. Also for the removal of tannic acids from solutions (*Jackson*). For either purpose an unadulterated article of commercial white lead is sufficiently pure, if it is completely soluble in solution of sodium hydrate.

LEAD CHLORIDE, $Pb\,Cl_2$.

USES. A saturated solution of lead chloride either in water or in solution of pure sodium chloride, in which it is more soluble, produces in solutions of the hydrochlorides of most alkaloids colorless, crystalline precipitates of double salts. Quinine and brucine in crystalline powder; morphine, codeine and cinchonine in needles; strychnine in felted fibres, etc. From these the alkaloids may be separated by $H_2\,S$ or by sulphuric acid (*Palm*). Also, in alcoholic solution, for the precipitation of albuminoids, even in the smallest traces (*Palm*). $Pb\,Cl_2 = 278.263$.

TESTS. Lead chloride forms long, colorless, rhombic prisms soluble at 15°C. in 105 parts of pure water (requiring up to 135 parts, if a little hydrochloric acid is present); at 100°C. in 33 parts of water. Absence of other metals is shown by the same tests as for metallic lead or lead acetate.

PREPARATION. A saturated solution of pure lead acetate in water is precipitated by a very slight excess of pure hydrochloric acid. The precipitate after washing is dissolved in boiling water and the crystals preserved, which separate on cooling.

LEAD CHROMATE, $Pb\,Cr\,O_4$.

USES. Fused lead chromate in fine powder is used for the oxidation of hydrogen and carbon in the ultimate analysis of organic compounds. It is thereby reduced to chromic oxide and a basic chromate. It is preferred before cupric oxide in the case of some non-volatile substances, which are more difficult to oxidize, and is sometimes used either jointly with cupric oxide or mixed with potassium dichromate.

TESTS. Lead chromate after fusion and powdering has a brownish-yellow color. Its most troublesome impurity is organic matter, accidently present through careless preservation. On heating to fusion it must yield neither carbon dioxide nor water, at a higher heat it must give off pure oxygen.

PREPARATION. A clear solution of 21 parts of crystallized lead acetate is precipitated by a solution of 16 parts of potassium dichro-

mate. The precipitate after washing and drying is fused in a hessian crucible, cast into thin plates and powdered while yet warm. It must be carefully preserved from dust and moisture. After use it may be regenerated by thorough washing, moistening with nitric acid and fusing. A current of oxygen may serve instead of nitric acid.

LEAD NITRATE, $Pb(NO_3)_2$.

USES. In some cases it is used as a substitute for lead acetate; in quantitative analysis it serves to oxidize arsenous into arsenic acid.

TESTS. Lead nitrate forms regular octohedral crystals, soluble in 2 parts of pure water. The tests for absence of other metals are the same as for other lead salts.

PREPARATION. Pure lead monoxide is dissolved in a slight excess of nitric acid and recrystallized from hot water.

LEAD OXIDES.

LEAD MONOXIDE, PbO, *Litharge.*

USES. Pure monoxide is used in quantitative analysis for the separation of phosphoric and arsenic acid, and, in conjunction with lead nitrate for that of arsenous acid. In assaying litharge, which needs not to be absolutely pure, is used for removing silica and as an oxidizing flux. It also serves to prepare pure metallic lead, etc.

TESTS. Other metals are to be detected by the same tests as for other lead salts. The following generally suffices: Metallic lead is found as a residue after solution in acetic acid; no effervescence must occur during this solution, showing absence of carbonate. The filtered solution is precipitated by dilute sulphuric acid in slight excess, and the precipitate filtered off. The filtrate, after addition of ammonia, must neither show a blue color (copper), nor a precipitate (iron, aluminium).

PREPARATION. On the larger scale litharge is obtained as a bye-product of the cupellation of argentiferous lead. Pure monoxide for the determination of arsenic is made by precipitating a solution of pure lead acetate or nitrate by ammonium carbonate, washing the precipitated carbonate and expelling CO_2 by ignition. It should be carefuly preserved, as it attracts CO_2 from the atmosphere.

RED LEAD, Pb_3O_4, is used as an oxidizing agent; to prepare chlorine from hydrochloric acid; to detect strychnine, and as a flux for oxidizing sulphides, etc., and for removing silicic acid by converting it into a fusible slag.

LEAD DIOXIDE, $Pb\,O_2$.

USES. For the separation of bromine from chlorine, especially in water analysis. The mixed haloid salts of the residue, from which iodine has been removed by palladious chloride or nitrate, are introduced into a retort, together with lead dioxide and acetic acid. Bromine is liberated and distils over, while the chlorides are not decomposed (*Wortmann*).

TESTS. The brown-purple powder must not yield anything soluble to nitric acid.

PREPARATION. A pure article of red lead is digested with an excess of nitric acid. and the process repeated as long as the nitric acid extracts anything. It is then thoroughly washed and dried.

LEAD HYDROXIDE or HYDRATE, $Pb\,(O\,H)_2$.

USES. Freshly precipitated hydrate dissolves to a small amount in pure water. This solution precipitates albumin, forming one of the most delicate reagents (*Palm*). The solid hydrate is sometimes used for the precipitation of tannic acid.

PREPARATION. Solution of pure lead acetate or nitrate is precipitated by an insufficient amount of potassium or ammonium hydrate, the precipitate thoroughly washed with boiled water and preserved free from contact with carbonic acid gas.

Litmus, see Color Reagents, page 84.

MAGNESIUM AND ITS COMPOUNDS.

MAGNESIUM, Mg.

USES. As it is more easy to obtain metallic magnesium free from arsenic than zinc, the metal is sometimes substituted for zinc to generate pure hydrogen with sulphuric or hydrochloric acid; from alkaline hydrates it does not liberate hydrogen; hence, it may be used to advantage in Marsh's or Gutzeit's arsenic test, but not in Fleitmann's, unless it has been platinized. When a few drops of platinic chloride solution are dropped upon magnesium it becomes coated with a thin film of platinum, and will now decompose even pure water. (The same process of platinizing is also applied to zinc and cadmium to render them more soluble in acids.) It may then also be used to great advantage for many reducing operations, e. g., to convert nitro-benzol into aniline (*Balle*). Magnesium also serves in the wet assay to precipitate lead (*Roessler*). As burning magnesium is very rich in the violet and ultraviolet rays, it is sometimes used as a source of light to detect fluorescent substances, e. g., quinine in urine. Mg. = 23.959.

TESTS When a small piece of pure magnesium is treated with pure dilute hydrochloric acid in a test tube covered with a cap of filter paper, upon which a drop of concentrated silver nitrate solution is placed, the color of the silver spot must not change to yellow or brown for an hour (absence of arsenic by Gutzeit's test). The solution in the tube, subdivided into several parts, must yield no precipitate with H_2S, nor, after neutralization by ammonia, with ammonium sulphide or carbonate. After precipitation by ammonium phosphate the filtrate must leave no residue after evaporation and ignition. The magnesium of commerce is generally pure from all other metals, except a trace of sodium, which is rarely objectionable, or some superficially adhering iron (from rusty rollers), which is easily removed by scraping.

PREPARATION. Seven parts of pure sodium chloride are fused together with 9 parts of potassium chloride, and, after cooling, are reduced to fine powder and intimately mixed with 96 parts of anhydrous magnesium chloride and 16 parts of fluorspar. A crucible, provided with cover, is heated in a furnace, and, as soon as it attains a bright red heat, 16 parts of metallic sodium are rapidly cut into small pieces, incorporated with the above mixture and put without delay into the crucible, which is then closely covered. A peculiar noise accompanies the reaction and, as soon as this is complete, the crucible is removed from the furnace. After the red glow has disappeared, but before the mass has solidified, the lid is removed and the small globules of magnesium are, by means of a clay pipe stem, collected to a single mass, the lid is then replaced and, after cooling, the metallic magnesium is freed from adhering slag by washing with water, and, if needed, even with a little dilute hydrochloric acid (*Fittig*). The metal has a silvery lustre and spec. grav. 1.75.

MAGNESIUM CARBONATE. $Mg\,C\,O_3 + 3\,H_2O$.

USES. This salt, as well as its basic compounds of various composition ($Mg\,C\,O_3 \,.\, Mg\,(O\,H)_2 + 3\,H_2O$ and $3\,Mg\,C\,O_3 + Mg\,(O\,H)_2 + 4\,H_2O$) is occasionally used in iron analysis and for saturation of acids instead of the oxide and hydrate; also for the preparation of other magnesium compounds. $Mg\,C\,O_3 = 83.813$.

TESTS. It is a light, white, flocculent substance of which only traces are soluble in water. In dilute acetic acid it must dissolve without residue. The solution, after expelling $C\,O_2$, must not be rendered turbid by H_2S nor by ammonium sulphide, carbonate or oxalate after addition of a sufficient amount of ammonium chloride and hydrate. It must be entirely free from sulphate or

chloride; hence, no turbidity must be produced by silver or barium nitrate.

PREPARATION. Cold saturated solutions of magnesium sulphate (4 vol.) and sodium carbonate (10 vol.) are mixed. After standing for a day or two, the precipitate is collected on a filter and washed with distilled water until the filtrate is no longer rendered turbid by barium chloride or silver nitrate. The product then consists of $Mg\,C\,O_3 + 3\,H_2\,O$. If made at higher temperature it loses $C\,O_2$ and contains various proportions of $Mg\,(O\,H)_2$.

MAGNESIUM CHLORIDE, $Mg\,Cl_2$.

USES. The anhydrous salt is used for the preparation of the pure metal. The hydrated, $Mg\,Cl_2 + 6\,H_2\,O$, serves instead of magnesium sulphate for the precipitation of phosphoric acid, where the introduction of a sulphate is objectionable. $Mg\,Cl_2 = 94.699$; $Mg\,Cl_2 + 6\,H_2\,O = 202.459$.

TESTS. It must be free from all other bases and from sulphate and phosphate. The absence of other bases is shown by the same tests as described for sulphate or carbonate. Its solution must not give a precipitate for several hours after being mixed with ammonium chloride and hydrate, nor with barium chloride. The crystals must dissolve without residue in 5 parts of concentrated alcohol. With sodium hydrate it must not yield ammonia vapor.

PREPARATION. The hydrate may be made by adding a slight excess of magnesium oxide to hydrochloric acid, shaking up frequently, filtering and evaporating, but not to dryness. The crystals obtained must be protected from moisture. The anhydrous salt is made by adding to the above solution twice as much ammonium chloride as there had been used of magnesium oxide, evaporating to dryness and then igniting at as low a temperature as possible to expel all the ammonium chloride. The salt must be carefully protected from moisture.

Magnesia mixture (*with chloride*) for precipitating phosphoric acid is made by dissolving 1 part of $Mg\,Cl_2 + 6\,H_2\,O$ and 2.5 parts of ammonium chloride in 10 parts of pure water and adding 5 parts of ammonia water, and filtering after standing for several days.

Magnesium hydrate, $Mg\,(O\,H)_2$, is occasionally used in the search for alkaloids for the removal of ammonia, amines and volatile ptomaines (*Tamba*). For this purpose it is precipitated from magnesium sulphate by an alkaline hydrate and used after thorough washing.

MAGNESIUM OXIDE, Mg O.

USES. The oxide, also known as *calcined magnesia*, is occasionally used in the analysis of iron, for the removal of phosphoric and arsenic acid, etc., and for preparing other magnesium salts. Mg O = 39.919.

TESTS. In dilute acetic acid it must dissolve without effervescing or leaving any residue. This solution must yield no precipitate with H_2 S; after addition of ammonium chloride and hydrate in slight excess no precipitate must fall (abs. of phosphoric acid, aluminium, etc.); nor must further addition of ammonium sulphide or oxalate produce either precipitate or color. After precipitating from the acetic solution all the magnesia by addition of ammonium hydrate and phosphate, the filtrate must, after ignition, leave no residue. The solution in nitric acid must yield no precipitate with the nitrate of barium or silver. It requires about 55000 parts of water for solution.

PREPARATION. Magnesium carbonate is heated to a red heat, in a suitable crucible, until all carbon dioxide has been expelled. It must be carefully protected from moisture and air.

MAGNESIUM SULPHATE, Mg S O_4 + 7 H_2 O.

USES. For the detection and quantitative determination of phosphoric and arsenic acids, which are precipitated as double salts of ammonium and magnesium. For this purpose a solution of magnesium sulphate, ammonium chloride and hydrate is usually employed under the *name of magnesia mixture;* also for the precipitation of globulin and its separation from albumin (*Hammarsten*). Also for testing ammonium sulphide for presence of free ammonia or carbonate (see page 39). Mg. S O_4 + 7 H_2 O = 245.403.

TESTS. Pure magnesium sulphate forms transparent, rhombic prisms, soluble in 0.8 parts of cool and in 0.15 parts of boiling water, insoluble in alcohol. Its reaction is neutral. Its solution in water, after acidulation with acetic acid, must not be precipitated by H_2 S; after addition of ammonium chloride and hydrate in slight excess no precipitate must fall, nor must the further addition of ammonium sulphide or oxalate produce either color or precipitate even after some length of time. Silver nitrate must produce no precipitate. The flame must not show the sodium reaction. After precipitating the watery solution of magnesium sulphate by ammonium phosphate and hydrate the filtrate must leave no residue on ignition.

PREPARATION. Epsom salt, selected as pure as obtainable, is dissolved in boiling water, digested for some time with a small

amount of magnesium oxide, filtered, crystallized in small crystals and recrystallized, if necessary.

Magnesia mixture is made by dissolving 1 part of magnesium sulphate and 2 parts of ammonium chloride in 8 parts of water, adding 4 parts of ammonia water and filtering after the mixture has stood for several days in a closed vessel.

Magnesium sulphide, $Mg\,S$ and *hydrosulphide*, $Mg\,(S\,H)_2$ are sometimes used to prepare sulphuretted hydrogen free from arsenic, by heating them while moist (*Divers* and *Shimidzu*). The sulphide is prepared by heating to redness an intimate mixture of magnesium sulphate and lampblack. The hydrosulphide is made by mixing an alkaline sulphide with magnesium sulphate. The mixture on moistening and heating gently gives off $H_2\,S$ in a regular current (*Gerhard*).

MANGANESE COMPOUNDS.

MANGANESE DIOXIDE, $Mn\,O_2$.

USES. For the preparation of chlorine, bromine, iodine, oxygen, manganates and permanganates, etc.; also for absorbing gases (hydrogen sulphide, sulphur dioxide). $Mn\,O_2 = 85.826$

TESTS. The native mineral varies considerably in composition. Some varieties have a large percentage of $Mn\,O_2$, and but a small amount of lower oxides of manganese and iron, while others are of low grade, containing carbonates, silicates, etc. The dark gray crystals of pyrolusite, containing 90% or more of $Mn\,O_2$, should be selected in preference to the soft, black varieties. Freedom from carbonates should be tested for by acetic acid; which should not produce effervescence. Its percentage of available oxygen may be readily ascertained by *Fresenius and Will's* method, in their two-flask apparatus, by converting oxalic acid by means of manganese dioxide and sulphuric acid into $C\,O_2$, and ascertaining its amount by loss of weight ($Mn\,O_2 + H_2\,S\,O_4 + H_2\,C_2\,O_4 = Mn\,S\,O_4 + 2\,H_2\,O + 2\,C\,O_2$).

MANGANOUS SULPHATE, $Mn\,S\,O_4 + 7\,H_2\,O$.

USES. For the titration of boracic acid, which it precipitates as manganous borate, $Mn\,B_2\,O_4$, insoluble in alcohol (*Edg. F. Smith*). Also for the detection of chromates in presence of dichromates by the brownish-black precipitate of manganese chromate (*Donath*), $Mn\,S\,O_4 = 149.73$.

TESTS. Manganous sulphate at different temperatures crystallizes with different amounts of water. Below 6° C. $Mn\,S\,O_4 + 7\,H_2O$

forms in pink colored, monoclinic prisms; above 7° C. and below 19° C. triclinic prisms of red color, containing 5 H_2O; between 20° C. and 30° C. monoclinic prisms with 4 H_2O; above that temperature still less water, in colorless crystalline powder, of but slight solubility. It must not give the iron reaction with potassium ferrocyanide.

PREPARATION. On a large scale it is obtained generally as a bye-product of other manufactures. It may be made by heating in a crucible the purest dioxide with a slight excess of sulphuric acid, until all the free acid evaporates; then raising the heat for a short time to redness so as to decompose the iron sulphate. The residue is leached out with water and recrystallized for purification.

Manganates and *permanganates* are described under their resp. bases, see *potassium salts*, etc.

MENTHOL, $C_{10}H_{20}O$.

USES. To detect glucose in urine, etc. With carbohydrates and concentrated sulphuric acid it produces a red color. Hence, a few drops of a 15% solution of menthol in alcohol are added to the liquid to be tested and conc. H_2SO_4 poured into it, so as to form a layer beneath. If glucose or a glucoside or carbohydrate is present the zone of contact assumes a cherry-red color (*Molisch*).

TESTS. The colorless or white crystals melt at 42° C. and boil at 212° C. At 100° C. they volatilize, and, if pure, leave no residue. When heated with a mixture of 2 parts of concentrated sulphuric acid and 1 part of water the melted menthol becomes at first brownish-red and finally deep blue, while the acid assumes a red brown color. The commercial article sold as "pip-menthol" is sufficiently pure.

PREPARATION. Pure oil of peppermint is solidified by a freezing mixture and reduced to —22° C. The solid is placed upon a funnel and slowly permitted to assume the surrounding temperature. A portion becomes liquid again and drains away, while the crystals remain on the funnel.

MERCURY AND ITS COMPOUNDS.

MERCURY or QUICKSILVER, Hg.

USES. For the preparation of its various salts. For amalgamation of copper, tin, sodium, zinc, etc. For filling tubes, etc., in a number of experiments, especially in gas analysis, where a heavy liquid is required to confine gases or liquids and keep them separated from each other. Hg = 199.712.

TESTS. A small drop, heated in a porcelain capsule, must volatilize without residue. When boiled for 1 minute with a concentrated aqueous solution of pure sodium hyposulphite it must not become tarnished. When rolled over white paper it must leave no trail. A solution of ferric chloride, shaken for some minutes with mercury, must not indicate any reduction by giving with potassium ferricyanide a blue precipitate. It must dissolve without residue in dilute nitric acid and, after precipitation by H_2S, the filtrate must, on evaporation, leave no fixed residue. Very dilute nitric acid is digested at ordinary temperature with an excess of mercury until saturated. Some of the solution is then precipitated by a slight excess of hydrochloric acid and rapidly filtered. The precipitate must not yield any lead chloride to boiling water, nor silver chloride to ammonia. The filtrate must give no precipitate with hydrogen sulphide.

PREPARATION. Pure mercury is best made from the crude commercial by distillation, an apparatus being employed for distillation under reduced pressure. For most purposes of gas analysis mercury may be purified sufficiently by digesting for several days with dilute nitric acid, washing, drying by blotting-paper and then pressing through chamois leather.

MERCURIC CHLORIDE, $HgCl_2$.

USES. Mercuric chloride, also called corrosive sublimate, is used for the detection and quantitative determination of small traces of arsenic, which are liberated as arsenetted hydrogen and passing through a solution of mercuric chloride deposit all of their arsenic as a yellow or brown compound with mercury (Mayençon and Bergeret). Also for the detection and volumetric determination of iodides, producing with them scarlet HgI_2. It yields up its chlorine either partly or entirely to reducents (Ag, Sb, As, Bi, Sn, As, Fe), and is thereby converted into mercurous chloride and finally into metallic mercury. Hence, it serves to detect tin, which it converts from stannous to stannic chloride; also formic acid, etc., etc. It precipitates some of the alkaloids (strychnine, colchicine, etc.); also gelatine and albuminoids as mercuri-albuminate. The latter reaction is most sensitive when the double salt $HgCl_2 + 2\,NaCl$, mixed with citric acid, is employed (*Stuetz*). It is also used to detect ammonia and ammonium carbonate by forming with them a white precipitate of mercur-ammonium chloride. For other ammonia salts the oxychloride (*Bohlig's reagent*) is used. It also serves to distinguish alkaline carbonates, which produce a red-brown precipitate of basic mercuric carbonate, from di-carbonates, which give no

precipitate. It is also used as a microchemical reagent to coagulate and harden certain tissues and render them more visible under the microscope. Also to prepare a number of mercurial compounds, mercuric iodide, Nessler's test, Bohlig's and Mayer's solutions, etc. $Hg\ Cl_2 = 270.452$.

TESTS. Sublimed mercuric chloride forms transparent crystalline crusts. When obtained from solution it forms rhombic crystals with acute terminals. It dissolves at 15° C. in 16 parts of water, in 3 parts of alcohol, of spec. grav. 0.820, or in 4 parts of ether; also in 2 parts of boiling water, or 1.2 parts of boiling alcohol. The solution in water reacts acid, but becomes neutral on addition of Na Cl. In the above solvents it must dissolve without residue. With Fleitmann's, or similar tests, it must not give any arsenic reaction. After precipitation of its aqueous solution by $H_2\ S$ no residue should remain by evaporating the filtrate, nor should the precipitate yield anything soluble to ammonia.

Commercial corrosive sublimate often contains a small amount of calomel, while otherwise pure. Such an article may be used for all solutions; but for decinormal volumetric solution the titre must be adjusted, or pure, recrystallized mercuric chloride taken.

PREPARATION. On the large scale the salt is made by sublimation of mercuric sulphate mixed with sodium chloride, and this process may be imitated on the small scale with pure salts. The commercial product may be purified by recrystallization from boiling water, or from alcohol, if it does not completely dissolve in the latter. The test solution contains one part of mercuric chloride in 20 parts of water.

Deci-normal solution contains 13.52 grammes of mercuric chloride in 1 litre, the solvent consisting of 4 parts of water and 1 part of alcohol. It is used for the titration of K I; as long as more than 2 K I are in solution for each $Hg\ Cl_2$ added, the red precipitate of $Hg\ I_2$ redissolves, forming $Hg\ I_2 . 2\ K\ I$; but as soon as the $Hg\ Cl_2$ exceeds this proportion, by even a single drop, the red precipitate remains undissolved and indicates the end of the reaction: $4\ K\ I + Hg\ Cl_2 = 2\ K\ Cl + Hg\ I_2 . 2\ K\ I$.

A solution of *mercuric oxychloride* is sometimes employed as *Bohlig's reagent* for the detection of ammonium salts. It is made by adding to a solution of 1 part of $Hg\ Cl_2$ in 30 parts of water, drop by drop, with constant agitation, a solution of 1 part of potassium carbonate in fifty parts of water, until the mixture ceases to redden litmus paper. The brown-red precipitate is filtered off; the clear filtrate indicates the presence of ammonium salts by a white precipitate.

MERCURIC CYANIDE, $Hg\,(C\,N)_2$.

USES. For the volumetric determination of glucose, which in alkaline solution reduces it to metallic mercury (*Knapp*).

TESTS. The salt crystallizes in colorless quadratic prisms, soluble in 12.8 parts of water at 15° C., in three parts at 100° C.; somewhat less soluble in alcohol. With potassium cyanide it forms a soluble double salt, $Hg\,(C\,N)_2\,.\,2\,K\,C\,N$. Its watery solution should not turn turmeric paper brown. With a very dilute solution of potassium iodide, added drop by drop, it should not yield a red precipitate of $Hg\,I_2$; after acidulation with nitric acid its solution should not give a precipitate with silver nitrate. At an elevated temperature it should separate into gaseous cyanogen, brown solid paracyanogen and metallic mercury, and should finally at 860° C. volatilize without residue.

PREPARATION. Mercuric oxide is dissolved in a slight excess of hydrocyanic acid, concentrated by evaporation at a low temperature in the dark, and the crystals carefully protected from light.

Knapp's volumetric solution contains 10 grammes mercuric cyanide and 12.5 gr. sodium hydrate, dissolved in water to make 1 litre. One decigramme of glucose reduces 40 Cc. of the solution. Ammonium sulphide is used as indicator by the method of "spotting."

MERCURIC IODIDE, $Hg\,I_2$ and MERCURIC POTASSIUM IODIDE, $Hg\,I_2\,.\,2\,K\,I$.

USES. Mercuric iodide is used to make a permanent iodized starch solution, to serve as indicator, by triturating 0.1 gr. $Hg\,I_2$ with 5 gr. of starch and some water, and, after solution, diluting to 1 litre (*Gastine*). The double salt, called also potassium iodohydrargyrate, in neutral alkaline and acid solution, finds many applications in analysis. Neutral, as *Mayer's solution*, it serves for volumetric determination of alkaloids. Also for indicating the completion of the fermentation process of beer, as young beer gives only a slight turbidity, while old, ripened beer gives a copious precipitate with the reagent (*Johanson*). In alkaline solution it serves either as *Sachse's solution* for volumetric determination of glucose or as *Nessler's test* for detection and colorimetric determination of ammonia, especially in drinking water. In acid solution it is used as *Geissler's test* for detection of minute quantities of albumin and in milk analysis for the precipitation of all albuminoids (casein, etc.), preparatory to determining the lactose by polarization. $Hg\,I_2 = 452.826$; $Hg\,I_2\,.\,2\,K\,I = 783.978$.

TESTS. Mercuric iodide forms a scarlet powder or quadratic crystals. It is insoluble in water, soluble in alcohol, acetic acid

and aqueous solutions of mercuric chloride or potassium iodide, forming with them colorless solutions. It should completely volatilize and give the other tests of purity from foreign metals, as described under mercuric chloride. In most cases it is used as prepared by potassium iodide and mercuric chloride, without separating the potassium chloride formed.

PREPARATION. Solutions of 10 parts of mercuric chloride and of 12.25 parts of potassium iodide are mixed, the precipitate collected on a filter, washed and dried.

MAYER'S SOLUTION is made of decinormal strength, and contains 13.546 gr. mercuric chloride and 49.8 gr. potassium iodide in 1 litre. It precipitates most alkaloids, forming with them generally crystalline compounds either of the formula Alk I_2 . Hg I_2, as aconitine, nepaline, atropine, hyoscyamine, coniine, nicotine, emetine, colchicine, etc., or of the formula Alk I . H I . Hg I_2, as strychnine, brucine, morphine, narcotine, quinine, cinchonine, etc., etc.

Occasionally, a solution of one-half the strength is employed (*Lyons*).

SACHSE'S SOLUTION contains in 1 litre 18 gr. Hg I_2, 25 gr. K I and 50 gr. K O H, dissolved in water. Of this solution 40 Cc. are placed in a porcelain capsule, and the glucose solution added from a burette as in Fehling's process. It requires 0.1501 gr. of dextro-glucose to reduce the 40 Cc. of solution to metallic mercury. An alkaline solution of stannous chloride serves as indicator to show the complete reduction of Hg by spotting.

NESSLER'S SOLUTION for the detection and colorimetric determination of ammonia is made by mixing 50 gr. of K I, dissolved in 50 Cc. of hot water, with a hot solution of 25 gr. of Hg Cl_2 in 100 Cc. of hot water, adding to the turbid red mixture a solution of 160 gr. of K O H (or 120 gr. of Na O H) in 400 Cc. of water, and filling up, after cooling, with (distilled) water to 1 litre. The solution, after standing, deposits its surplus of Hg I_2, and may be decanted, but it is essential that a full saturation with Hg I_2 should be made, lest an excess of K I should redissolve the precipitate made by ammonia. Some direct 66.4 gr. of K I and 27.1 gr. of Hg Cl_2, so as to make the solution one-fifth normal. Of this solution 1 Cc. each is added in Nessler cylinders, having the 50 Cc. mark at equal height from bottom, to the specimen of water to be tested and to 4 specimens containing various amounts of standard ammonia solution. A reddish-yellow color indicates the presence of ammonia, and by comparison of the depth of color the quantity is estimated.

GEISSLER'S SOLUTION, for detecting and removing albuminoids, is made by dissolving 13.5 gr. $Hg\,Cl_2$ and 333.2 gr. K I in 20 Cc. acetic acid of spec. gr. 1.048 and 64 Cc. of water, and aiding solution by gentle heat. In this strength it serves to precipitate albuminoids from milk, of which various quantities are taken, according to its specific gravity, and obtaining a solution ready for determining lactose by the polariscope. For mere qualitative detection of albumen a much weaker solution is used, made by adding to the above amount 400 Cc. of water instead of 64 Cc.

MERCURIC NITRATE, $Hg\,(N\,O_3)_2$.

USES. In solution containing nitrous acid and but slight excess of nitric acid it serves to detect albuminoids, tannin, guaiacol, eugenol, vanillin, etc., by producing a red colored precipitate (*Millon's reagent*). Also for the precipitation of the albuminoids of milk preparatory to estimating lactose by polarization. For the volumetric determination of urea by *Liebig*'s method. $Hg\,(N\,O_3)_2 = 323.514$.

TESTS. Mercuric nitrate must not give a white precipitate with hydrochloric acid (abs. of mercurous salt, etc.). By heat it is first converted into red oxide and then completely volatilized. Tests for admixture of other metals are the same as for mercuric chloride. The salt may crystallize with various amounts of water. Solution of the perfectly neutral salt in water gradually decomposes it, and protracted boiling precipitates mercuric oxide.

PREPARATION. By dissolving pure mercury in a slight excess of hot conc. nitric acid and crystallizing.

Liebig's volumetric solution is made by dissolving 77.2 grammes of pure mercuric oxide in a slight excess of nitric acid and diluting to 1 litre. Each 1 Cc. corresponds to 10 Mgr. urea. In adding the solution to urine care must be taken to neutralize the liberated acid by repeated additions of sodium carbonate (calcium carbonate, *Pflueger*). A white precipitate of a compound containing 1 molecule of urea and 2 mol. of mercuric oxide, $C\,O\,(N\,H_2)_2 \,.\, 2\,Hg\,O$, falls as long as urea is present. As soon as it is all removed, the mercuric solution is converted into a reddish precipitate by the sodium carbonate used as indicator. Sometimes the chlorides are first removed by silver nitrate, an excess of which does not interfere (*Rautenberg*).

Millon's reagent is made by dissolving 1 part of mercury in 1 part of nitric acid, of spec. gr. 1.42 (up to 1.52), and, after complete solution by the aid of heat, adding an equal volume of water. It should contain $N_2\,O_3$, but no great excess of nitric acid. When, by long

preservation, nitrous acid has become deficient, the reagent is no longer sensitive, but may be restored by adding a little $K N O_2$. For removing albuminoids from milk a solution is used containing double the amount of nitric acid as Millon's solution (*Hoffmann's reagent*).

MERCUROUS NITRATE, $Hg_2 (N O_3)_2 + H_2 O$.

USES. For detecting some acids, especially those of the chlorine group, by characteristic precipitates. For separating phosphoric acid from bases (*H. Rose*). Also for oxidation of some reducents (formic acid, etc.), which separate from it metallic quicksilver. Also for detecting brucine, which, with mercurous nitrate free from excess of acid, gives a red color (*Flueckiger*).

TESTS. The salt forms transparent, monoclinic crystals, which, in water acidulated with nitric acid, dissolve without change, but are soon decomposed in solution in pure water, a yellow basic salt, $Hg_2(N O_3)_2 H_2O + H_2 O$, being deposited. Other basic salts form when metallic mercury is kept in contact with the neutral solution, but the formation of mercuric salt is thereby prevented. Light decomposes the salt. Addition of a slight excess of dilute hydrochloric acid should completely precipitate the mercury as calomel and leave in the filtrate no substance capable of being blackened by $H_2 S$ or of leaving a fixed residue on heating. Other tests are the same as for mercuric chloride.

PREPARATION. Equal weights of pure quicksilver and nitric acid of spec. gr. 1.2 (made by mixing 7 parts of water with 6 parts of pure nitric acid of spec. grav. 1.42) are placed for 24 hours in a porcelain capsule in a cool, dark room. The crystals are then separated, carefully drained and preserved in opaque bottles. For use they are dissolved in 10 parts of water containing about 5% of nitric acid, and the solution preserved in an opaque bottle containing a small amount of metallic mercury. When containing some free nitrous acid the solution is sometimes called *Plugge's* reagent.

MERCURIC OXIDE, $Hg O$.

USES. Precipitated mercuric oxide in fine powder is used for the separation of magnesium from the alkalies, by digesting their chlorides with it. Also in the volumetric determination of cobalt by *Winkler's* method for removing iron, manganese, etc. Also in the determination of nitrogen in organic bodies, according to *Kjeldahl's* method, as an addition to shorten the time of digestion with sulphuric acid; the mercury being subsequently removed by $H_2 S$. Also for separating uranium chloride from the chlorides of

other bases (*Alibegoff*). Also for the preparation of mercuric salts.

TESTS. It must volatilize without residue. The oxide prepared by precipitation in the state of a fine yellow powder is preferable to the red crystals obtained by the dry methods.

PREPARATION. To a hot, dilute solution of pure sodium hydrate, which must be kept in excess, a solution of pure mercuric chloride is gradually added. The yellow precipitate is thoroughly washed by decantation and preserved in the moist state.

Meta-phenylene-diamine, see *Color Reagents*, *m* diamido-benzol, page 78.

METHYL IODIDE, CH_3I.

USES. Its high specific gravity, = 2.1992 at 0° C., makes it useful in a set of reagents for petrographic separation. It is also used for the detection of pyridine bases. A few drops of the base are heated in a test tube with an equal amount of methyl iodide, and then mixed with a little powdered potassium hydrate and a few drops of water. On gentle heating a peculiar penetrating odor indicates a pyridine base (A. W. Hofmann). $CH_3I = 141.531$.

TESTS. The tests for purity need not be extended beyond identification of boiling point and specific gravity. The commercial article is sufficiently pure. Methyl iodide is a colorless liquid of ethereal odor, spec. gr. 2.1992, at 0° C. and boils at 44° C. When heated with 75 parts of water it is decomposed into hydriodic acid and methyl alcohol. It attracts moisture from air and forms a crystalline hydrate.

PREPARATION. One part of red phosphorus in small pieces and 5 parts of concentrated wood alcohol are placed into a flask and gradually mixed with 10 parts of powdered iodine. The product of the reaction is distilled off and rectified, preserving the portion boiling at 44° C.

METHYLENE IODIDE, CH_2I_2.

USES. On account of its specific gravity being 3.342 at 5° C. the liquid is used as a petrographic separator. $CH_2I_2 = 267.088$.

TESTS. The yellow liquid boils at 180° C., being partially decomposed, and congeals at 0° C., forming tabular crystals.

PREPARATION. Fifty gr. iodoform and 200 gr. concentr. hydriodic acid are heated to 127° C. and small pieces of phosphorus thrown in until the liquid is no longer colored brown; then more iodoform and phosphorus may be alternately added, hydriodic acid being regenerated (*Baeyer*). It may be purified by freezing and selecting the crystals.

Methyl Orange, see *Color Reagents*, Dimethyl-amido-azo-benzol-sulphonic acid, page 78.

Methyl Violet, see *Color Reagents*, page 85.

Methylene aceto-chlorhydrin has been proposed by *Grimaux* as a reagent for morphine. When the reagent is added to morphine in powder, or dissolved in glacial acetic acid, and then sulphuric acid in excess, a rose-red color is produced.

Millon's Reagent, see *Mercuric Nitrate*, page 133.

Molybdic Acid and derivatives, see page 12.

NAPHTHALIN DERIVATIVES.

NAPHTHOL, $C_{10} H_7 O H$.

USES. The two varieties called *Alpha* and *Beta-naphthol* are both used for the detection of chloroform and chloral hydrate, which, with solution of naphthol in potassium hydrate, heated to about 40° C., give a transient blue color (*Lustgarten*). Both in solution in conc. alcohol give various color reactions with dry powdered sugar and other carbohydrates (*Ihl*). These, however, are more delicately shown in *Molisch's* modification, by means of which very minute traces of sugar may be detected by alpha-naphthol (or naphthalin), but not by beta-naphthol. *Molisch* mixes a few drops of a 15% solution of alpha-naphthol in alcohol with the urine or other sugar solution, and then adds concentr. sulphuric acid, to form a layer beneath. At the zone of contact a violet color appears, even if but slight traces of sugar are present.

TESTS. The commercial articles are sufficiently pure; even naphthalin will answer as a substitute.

PREPARATION. A mixture of 4 parts of naphthalin and 3 parts conc. $H_2 S O_4$ is kept for 12 hours at the temperature of 80° C. and then poured into 10 to 12 volumes of boiling water. After cooling, the unchanged naphthalin is filtered off and the filtrate saturated with lead carbonate. On evaporation the beta-salt crystallizes first, the alpha afterwards. The mixed salts are boiled with 12 parts of alcohol, which dissolves the alpha, but leaves the beta-salt undissolved. From the separated lead salts the naphthalin-sulphonic acids are isolated by hydrogen sulphide. Heating with potassium hydrate liberates the naphthols corresponding to the acids.

NITROSO-beta-NAPHTHOL, $C_{10} H_6 . (N O) O H$.

USES. The solution in acetic acid serves for the separation of cobalt from nickel, its nickel salt being soluble, the cobalt salt in-

soluble in dilute hydrochloric acid (12%); also of iron from aluminium, the iron salt forming an insoluble precipitate, which, by heating with oxalic acid, is converted into ferric oxide, while aluminium remains in solution (*Ilinski and v. Knorre*). Also to separate copper from lead, cadmium, zinc, magnesium, etc (*v. Knorre*). At. W. = 172.681.

TESTS. The compound crystallizes either in short prisms or thin tablets of orange-brown color; melting at 109.5° C., almost insoluble in water, very soluble in ether, carbon-disulphide, glacial acetic acid and hot alcohol, somewhat less in cold alcohol and acetic acid of 50%. Its alkali salts are green; that of sodium is insoluble in weak soda lye.

PREPARATION. One part beta-naphthol and 0.75 parts of zinc chloride are dissolved in 6 parts of hot alcohol, and, after boiling a short time, 0.5 parts of sodium nitrite dissolved in a little water is added and the boiling continued until the red-brown zinc-nitroso-beta-naphthol begins to separate. After 12 hours' standing this is filtered off and washed with a little alcohol. The zinc salt is then diffused in 10 parts of water and gently heated with 1 part of sodium hydrate. This dissolves the zinc, while green sodium-nitroso-beta-naphthol separates in crystals. After cooling, the sodium salt is removed by filtration, washed with dilute sodium hydrate solution and decomposed by cold, dilute hydrochloric acid, which leaves the pure alpha-nitroso-beta-naphthol (*Ilinski and Henriques*).

NICKEL AND ITS COMPOUNDS.

NICKEL, Ni.

Metallic nickel is sometimes used in the form of capsules, instead of silver, for dissolving aluminium hydrate in alkaline hydrates so as to separate it from ferric hydrate. Also in the form of wire in blowpipe work. Also for the preparation of nickel salts. Ni = 57.928.

NICKELOUS CHLORIDE, $Ni\,Cl_2 + 6\,H_2O$.

USES. As an indicator in the volumetric determination of zinc by sodium sulphide. Also in conjunction with potassium hydrate for detection of glucose, as proposed by *Mazzara.*

TESTS. Commercial nickel chloride is sufficiently pure for the above purposes.

PREPARATION. The metal is dissolved by means of heat in hydrochloric acid and crystals obtained by evaporation.

NICKELOUS HYDRATE, *oxide* or *oxalate*, are sometimes used in blowpipe analysis, to detect potassium in presence of sodium and lithium by the blue color given to the borax bead, colored brownish by a nickel salt. The purity of the commercial article suffices for this purpose. The hydrate also serves for removal of tannin.

NICKELOUS SULPHATE, $Ni\,S\,O_4 + 7\,H_2\,O$.

USES. For volumetric determination of tannic acid an empyrical solution of nickelous sulphate is used with ferric chloride as indicator (*Casali*). The salt is also used as indicator by spotting in the volumetric determination of zinc by sodium sulphide. At. W. = 279.472; anhydrous $Ni\,S\,O_4 = 153.752$.

TESTS. Nickelous sulphate crystallizes at ordinary temperature in dark green, monoclinic prisms, containing $7\,H_2\,O$, but may be obtained between 30° and 40° C. in quadratic blue-green crystals with $6\,H_2\,O$, or at still higher temperature again in, monoclinic crystals with $6\,H_2\,O$. Hence, for quantitative work, it must be weighed in the anhydrous state, after drying at 270° to 300° C. Its solution must not become blue-black on addition of tannic acid, nor give a blue precipitate with potassium ferrocyanide. A borax bead saturated with it must not show the intense blue color of cobalt.

PREPARATION. Nickel sulphate is now sold quite pure, being manufactured on the large scale for electro-plating. To remove the remaining traces of copper, iron and cobalt it may be dissolved in water acidulated with a few drops of sulphuric acid, and digested for some time with a small bright piece of iron wire, to precipitate copper, if any be present. After filtering the iron is converted into ferric salt by heating with some nitric acid, and then removed by precipitating with a large excess of ammonia water in which nickel redissolves, leaving ferric hydrate behind. The filtrate is evaporated to dryness and heated to 300° C. to expel ammonia. It is then redissolved in water acidulated with acetic acid and the cobalt precipitated by potassium nitrite. The yellow precipitate of potassio-cobaltic nitrite (Fischer's salt) is allowed to subside for 24 hours and then removed by filtration. In the filtrate the nickel is then precipitated by sodium carbonate, the precipitate thoroughly washed, dissolved in sulphuric acid and crystallized.

Casali's volumetric nickel solution is made by dissolving 2.89 gr. of pure anhydrous nickel sulphate in boiling water acidulated with a few drops of sulphuric acid. After cooling, a solution of

30 gr. of ammonium sulphate is added. The solution is divided into two equal parts, and to one-half ammonia water is added, drop by drop, until it has assumed a violet-blue color. The two solutions are then mixed and diluted to 1 litre. One Cc. precipitates 0.01 gr. of pure tannic acid from galls, or 0.01497 gr. of oak bark tannin (quercotannic acid and phlobaphen, etc.) Paper moistened with ferric chloride serves to indicate the complete precipitation of tannin.

NITROUS ETHER or *ethyl nitrite*, $C_2H_5 . NO_2$, may be used, on account of its nitrous acid, to detect antipyrine by the green color of the iso-nitroso-antipyrine produced by adding to it nitrous ether and some free acid. Also to detect phenol and salicylic acid by the yellow color of the nitro-compound formed, and albumen by the formation of yellow xanthoprotein (*Eyckmann*). U. S. P. spir. ætheris nitrosi will answer the purpose.

OILS are occasionally used for analytical purposes:

Linseed oil to absorb vapors of carbon disulphide;

Sweet almond oil as a solvent, and to differentiate in microscopical research between coloring matters soluble in it (saffron), from those insoluble (safflower);

Poppy oil to detect turpentine as an adulterant of essential oils;

Oil of turpentine to aid in the detection of blood by guaiacum (*Van Deen*), etc.

Osmic acid, see page 15.

OXYGEN, O.

USES. Pure, dry oxygen gas is used for combustions in elementary organic analysis. $O = 15.96$.

TESTS. Absolute purity from carbon dioxide and chlorine is requisite; hence, the gas passing through lime water and through silver nitrate solution must not render them turbid. Moisture must be removed by passing it through dry calcium chloride, or conc. sulphuric acid, or both. Nitrogen may be present from incomplete expulsion of air from the generating or storing apparatus; its presence and quantity is ascertained by enclosing a measured volume of the gas in a graduated tube over mercury and absorbing the oxygen by potassium hydrate and pyrogallic acid. If no portion is absorbed by solution of potassium hydrate alone (CO_2), and the whole is then absorbed after introduction of the pyrogallic acid, the oxygen is pure; if not, the percentage of remaining nitrogen is noted and allowed for in calculating the results of the combustion.

PREPARATION. It is best to prepare sufficient to serve for several occasions, so as to avoid the necessity of losing from each small portion the quantity necessary to expel air from the apparatus. It is made by carefully and very gradually heating an intimate mixture of 20 parts of pure potassium chlorate with one part of pure manganese dioxide in a copper flask with metallic delivery tube and ground joint connections. (See also potassium chlorate). A wash bottle is introduced containing a dilute solution of caustic soda, and the tube leading from it to the gasholder is so arranged that the first portion of gas generated can escape for a sufficient length of time to insure expulsion of air from all parts of the apparatus. The gas is then received into the holder, which is filled completely with water, from which dissolved gases have been expelled by boiling. When the gas is to be transferred into the combustion tube similar precautions for expulsion of air must be taken, as it must pass through apparatus interposed between the holder and the tube, which contains absorbents retaining chlorine, carbon dioxide and moisture, so that only pure, dry gas may reach the combustion tube. Potassium chlorate yields 39.18% of its weight of oxygen; 100 grammes yield 27.4 litres.

Oxygen may also be obtained from hydrogen dioxide solution by the addition of potassium permanganate; 100 Cc. of the usual 3% commercial solution of H_2O_2 furnishing one litre of oxygen (*Goehring*).

PALLADIUM AND ITS COMPOUNDS.

PALLADIUM, Pd.

USES. In gas analysis metallic palladium in the form of thin foil or wire, or as a finely divided metallic coating of asbestus, etc., serves to absorb free hydrogen from gas mixtures, and thus to measure its quantity by contraction of volume. This absorption takes place after the metal has, by heating in air, been superficially coated with a thin film of palladious oxide. During the absorption the metal becomes hot and cools again as soon as all the hydrogen has been occluded. If air be now readmitted the occluded hydrogen unites with its oxygen, liberating heat enough to set the metal aglow, and, after the disappearance of the hydrogen, the film of oxide is restored, making the palladium ready for another operation. The process is conducted in a narrow glass tube, bent into suitable shape, interposed between the gas burette and pipette. Sometimes a measured volume of air is added at once to the mixture of gases and the palladium in the tube

heated by a water bath, while the gases are slowly passed over it, effecting a quiet combustion of the hydrogen in contact with the metal (*Winkler*, *Hempel*).

Palladium, fully charged with occluded hydrogen by connecting it with the positive pole of a galvanic battery and immersing it into dilute sulphuric acid, is used to reduce metals from their solutions, and thus to make quantitative determinations of copper and gold, etc. (*Schwartzenbach and Kritschewsky*). For these uses the metal furnished by the platinum affineries is sufficiently pure. See also *palladium-asbestus*, on page 46. Pd = 105.735.

TESTS. Pure palladium dissolves without residue in warm, fuming nitric acid. It does not yield anything soluble to cold, dilute sulphuric acid. In nitro-muriatic acid it dissolves without residue.

PALLADIOUS CHLORIDE, $Pd\,Cl_2$.

USES. Palladious chloride and its double salt *sodium-palladious chloride*, $Pd\,Cl_2 . 2\,Na\,Cl$, are used for detection and quantitative determination of iodine, which is precipitated from iodides as brown-black palladious iodide, $Pd\,I_2$, insoluble in water, while bromides are not precipitated. Paper or cloth strips, immersed in dilute solution of palladious chloride (2 Mgr. in 1 litre of water), are blackened by $C\,O$, $H_2\,S$, $C\,H_4$, $C_2\,H_6$, H ozone and $N\,H_3$ (?), while $C\,O_2$, N, O, Cl, $N_2\,O_3$ and cyanogen are without effect (*Boettger*, *Fodor*, *Schneider*).

Palladious chloride and sodium-palladious chloride is also used for the detection, removal and quantitative determination of carbon monoxide, absorbed by cuprous chloride from mixtures of gases. The pure solution of cuprous chloride does not affect the palladium solution, but as soon as it contains C O it reduces and precipitates metallic palladium: $Pd\,Cl_2 + C\,O + H_2\,O = Pd + C\,O_2 + 2\,H\,Cl$. Each 1 gr. of Pd = 0.2641 gr. = 211 Cc. of C O.

A mixture of the two solutions, palladious chloride and cuprous chloride, both saturated with sodium chloride, may be used to first absorb the C O and then convert it into $C\,O_2$, which may be determined by absorption in K O H in the gas pipette and thus volumetrically determined (*Winkler*). $Pd\,Cl_2$ = 176.477.

TESTS. Pure anhydrous palladious chloride is a brown mass, which attracts moisture from air; it dissolves easily in water, from which, on evaporation, it crystallizes in quadratic prisms, containing $Pd\,Cl_2 + 2\,H_2\,O$, which no longer attract water. After precipitation by an excess of pure potassium iodide from a solution acidulated with hydrochloric acid, the filtrate should not give more

than mere traces of a precipitate with hydrogen sulphide or ammonium sulphide. Its solution gives a brownish precipitate with potassium hydrate, which redissolves on addition of an excess of the alkali. From this solution alcohol reduces metallic palladium. Ammonium chloride in concentrated solutions produces a flesh-colored precipitate soluble in ammonia water.

PREPARATION. Pure palladium is dissolved in nitro-muriatic acid, the clear solution is evaporated to expel the excess of acid, then redissolved in water and crystals obtained by evaporation. These for use are dissolved in 10 parts of water. *Sodium-palladious chloride* is made by adding 6 parts of pure sodium chloride for every 5 parts of metallic palladium dissolved in the nitro-muriatic acid, evaporating to dryness and dissolving in 12 parts of water (Fresenius).

PALLADIUM NITRATE, $Pd(NO_3)_2$, has been proposed for the detection of bromides. In concentrated neutral solution it gives with bromides a red-brown precipitate of $PdBr_2$, while palladious chloride gives none; iodides, however, are precipitated by it, as well as by palladious chloride. Hence, after precipitation of the iodides by $PdCl_2$ and neutralization, bromides may be detected in the filtrate by palladious nitrate. The method is not much in use. $Pd(NO_3)_2 = 229.539$.

It is made by dissolving palladium in concentrated nitric acid.

PARAFFIN.

Paraffin of commerce consists of a mixture of various hydrocarbons of the general formula C_nH_{2n+2}, with others of the olefine series. It is sold in different states of consistence—solid, semi-solid and liquid (paraffin oil). The *solid* is sometimes used to prepare hydrogen sulphide by heating it together with sulphur. The *semi-solid* serves as a valuable lubricator for glass apparatus: ground joints, stoppers and stopcocks. *Liquid paraffin* is a ready solvent of chlorine, bromine, iodine, colorless phosphorus, etc.; hence, it is used in the preparation of some of their compounds, hydriodic acid (see page 7), hydrobromic acid, phosphorus compounds and haloid ethers. With chloroform and ether it forms clear solutions when they are anhydrous, but turbid if they contain water; hence, it may be used to detect its presence in them (*Leon Crismer*). It absorbs gaseous hydrocarbons, and its use is, therefore, proposed in gas analysis (*Hasenpflug*). Liquid paraffin, as well as solid, is also used to prepare hydrogen sulphide by heating it with sulphur (*Lidoff*). The liquid paraffin used for these purposes must be colorless, free from fluorescence, its spec.

grav. not less than 0.840; it must not contain volatile constituents boiling below 360° C. Freshly cut metallic potassium or sodium must not lose its lustre when immersed in it for some time. When kept at 100° C. in contact with conc. sulphuric acid it must not within 24 hours either become brown itself or communicate to the acid more than a light brown color.

PARALDEHYDE, $(C_2H_4O)_3$, has been recommended by *Amthor* for detection of caramel in wine, etc. When paraldehyde is added in sufficient quantity to wine colored with caramel a brown precipitate forms, while the liquid becomes colorless. Natural wines give a white precipitate. The paraldehyde of commerce is sufficiently pure for this reaction.

PARA-TOLUIDINE, $C_6H_4 . CH_3 . NH_2$.

USES. The commercial salt, containing ortho-toluidine and aniline, is used for the detection of nitric acid, even in small traces, as in natural waters. When a few drops of a solution of para-toluidine in sulphuric acid are mixed with several Cc. of water containing a nitrate, and then concentrated sulphuric acid added, so as to form a layer beneath, the zone of contact assumes a red color, which gradually fades into yellow. Chlorates, bromates, iodates, chromates and permanganates produce a blue color with the reagent, so intense as to hide the red of nitrates, if simultaneously present. With nitrous acid the color is yellow to brown, according to the quantity present (*Longi*). The absolutely pure salt gives with nitric acid a blue color, which gradually passes into red, while the impure commercial gives the red at once. See also Aniline Sulphate, page 42.

TESTS. Pure para-toluidine crystallizes in colorless tables; melts at 45° C.; boils at 198° C. It dissolves in 285 parts of water at 12°. Chlorinated lime solution does not color it blue or violet, if aniline is absent.

PREPARATION. The pure salt may be made by distilling the commercial, preserving the fraction boiling between 195° and 205° C., and cooling it to 0°; this separates most of the ortho-toluidine, which remains liquid to —20° C. Two parts of the crystals are then dissolved in 8 parts of boiling water; 1 part of oxalic acid is added and the solution cooled to 80°. Para-toluidine oxalate precipitates, while the aniline salt remains in solution. The precipitate is filtered off, washed with ether to remove the last trace of ortho-toluidine, and the pure oxalate is then decomposed by distilling with calcium hydrate.

PHENOL, $C_6H_5 . OH$.

Carbolic Acid.

USES. For detecting nitric acid, by which phenol is converted into the intensely yellow tri-nitro-phenol, picric or carbazotic acid, whose color may be still more heightened by converting it into the ammonium salt. Drinking water or other liquids containing traces of nitrates are evaporated to dryness and moistened with a drop of a mixture of 1 part phenol, 4 parts of concentrated sulphuric acid and 2 parts of water. In conjunction with mercurous nitrate, phenol serves to detect nitrous acid by precipitation of metallic mercury and a red color of the solution (*Plugge*). It is also used for the detection of wood pulp in paper, which turns yellowish-green when moistened with a solution of 1 drop of liquid phenol in 1 Cc. of hot concentrated hydrochloric acid (*Ihl*). Phenol has also been proposed to detect adulterations of butter with other fats. If 1 gr. of butter is melted with 3 gr. of deliquesced phenol, and then 900 Cc. of water added, and the mixture gently heated, the solution must remain clear and uniform, if the butter is pure (*Crook*). Conjointly with sulphuric acid, phenol serves to detect, by the red color produced, colocynthin (*Johannson*) and elaterin (*Lindo*); narceïne, veratrine, codeïne, etc. (*Arnold*); also sugars by a reddish-brown (*Molisch*). It also serves to detect glycerin in wine, etc., by heating the solution to dryness, moistening with a drop or two of a mixture of equal parts of phenol and concentrated sulphuric acid and adding ammonia. A red color indicates glycerin (*Donath and Mayrhoffer*). A standardized solution of phenol is also used for titration of bromine, with which it precipitates as tri-brom-phenol (*Giacosa*).

As the violet color, which is produced when phenol is mixed with neutral ferric chloride, does not appear in presence of glycerin, this reaction may serve to detect the latter. The liquid is diluted with water and very little phenol is added; if, on addition of one drop of ferric chloride, no violet color appears, glycerin is present (*Barbsche*).

It also, in conjunction with calcium hydrochlorite, serves to detect ammonia by a green color (*Lex*).

Phenol-potassium serves for the identification of iodoform in urine, etc. The liquid is mixed with a little alcohol and a few drops of it poured upon a small quantity of phenol potassium in a test tube and gently heated. A red coating will cover the bottom of the test tube, soluble in dilute alcohol (*Lustgarten*).

$C_6H_5 . OH = 93.804$.

TESTS. Pure phenol crystallizes in colorless, rhombic needles, melting at 40° to 41° C. Phenol hydrate, $(C_6H_5 . OH)_2 + H_2O$, melts at 16° C. Presence of water or of cresol, or other homologues, changes the melting point. It boils at 183°. At 16° it dissolves in 15 parts of water; at 87° it is miscible with it in all proportions. It easily dissolves in alcohol and ether. The watery solution reddens litmus slightly. Traces of ammonium nitrite (often found in the atmosphere) color it red. With H_2S it must produce neither color nor precipitate. The purest white crystals of commerce, though not entirely free from homologues, are sufficiently pure for making the reactions described above. The strength of solutions is ascertained by titration with bromine.

PREPARATION. Phenol is obtained on a large scale by fractional distillation of the "dead-oil" portion of coal-tar, saturating the product with caustic alkali to remove tarry matters, etc., decomposing again by acid to separate the phenol, which is further purified by repeating the process and by fractional distillation.

Phenol-potassium is made by dissolving 4 parts of potassium in 9.5 parts of phenol, in a vessel filled with hydrogen gas to prevent oxidation by the atmospheric oxygen. It forms needle-shaped crystals, which easily deliquesce and must be carefully preserved.

Phenol-phthalein, see *Color Reagents*, page 87.

PHENYL-HYDRAZINE, $C_6H_5 . NH . NH_2$.

USES. Phenyl-hydrazine and its hydrochlorate, $C_6H_5 . NH . NH_2 . HCl$, are used for the detection of aldehydes, ketones, and especially of sugars. The characteristic compounds formed with these differ in their melting points, so as to permit more special identification. Those with dextrose (phenyl-dextros-azon) and with levulose (phenyl-levulos-azon) melt at 204° C.; lactose, 200°; maltose, 206°; benzaldehyde (bitter almond oil) and cinnamic aldehyde at 152.5°; salicylic aldehyde at 142°; acetophenon at 170°, etc. (*E. Fischer*). For sugar in urine the reagent is especially valuable, as it is less liable to mislead than the various tests based upon reduction of metallic salts, there being no other substance in urine capable of producing phenyl dextros-azon. To 5 Cc. of urine a solution of 0.1 to 0.2 gr. of phenyl-hydrazine hydrochlorate and 0.15 gr. of sodium acetate in 2 Cc. of water is added and heat applied for several minutes, when golden-yellow phenyl-dextros-azon is precipitated, mostly in needle-shaped crystals (*Jaksch*). The test has been modified by *Schwarz*, who mixes 5 Cc. of urine with 5 Cc. of normal potassium hydrate, adds 1 or 2 drops of the free base, phenyl-hydrazine, and heats to boiling. If glucose is present, the solution

assumes an intense yellow or orange color. After cooling a slight excess of acetic acid is added, which precipitates the yellow crystals of phenyl-dextros-azon. $C_6H_5 . NH . NH_2 = 107.886$.

TESTS. Pure phenyl-hydrazine crystallizes in tabular crystals, which at 23° C. melt to form a yellow, oily liquid, which only congeals again at a much lower temperature. It boils at 233° to 234° C. In cold water it dissolves very sparingly, and is almost insoluble in solutions of caustic alkalies. It reduces salts of copper, silver, gold and platinum in the cold.

Phenyl-hydrazine hydrochlorate forms small, silky tablets, easily soluble in hot water, sparingly in cold, almost insoluble in concentr. hydrochloric acid. The commercial preparations are of sufficient purity.

PREPARATION. Dissolve 10 gr. aniline in 200 gr. conc. hydrochloric acid, cool the solution well and very gradually add a solution of 7.5 gr. sodium nitrite in 50 Cc. water. Some sodium chloride is precipitated, and the solution contains diazo-benzol chloride; it is filtered and then an ice-cold solution of 45 gr. stannous chloride in 45 gr. conc. hydrochloric acid is added. Phenyl-hydrazine hydrochlorate is formed at once, and separates in minute white crystals, which are removed by filtration. From these the pure base may be made by dissolving in warm water, adding sodium hydrate sufficient to combine with the acid, removing that part of the oily base which separates and, finally, extracting the rest by shaking out with ether (*V. Meyer and Lecco*).

Phloroglucin, see Color Reagents, page 87.

PHOSPHORUS, P.

USES. The ordinary colorless, transparent variety is used in gas analysis, in the form of thin pencils, for absorption of oxygen (*Lindemann*). Also for making various preparations of phosphorus, red phosphorus, the oxides and acids, the various halogen compounds of phosphorus, etc.; it is also used for the preparation of hydriodic acid, methyl iodide, etc., for which, however, red phosphorus is preferable. $P = 30.958$.

TESTS. Pure phosphorus of the ordinary variety is of waxy consistence, transparent, colorless, or slightly yellow; it melts at 44°, ignites at 50°, insoluble in water, sparingly soluble in absolute alcohol or ether, easily in carbon disulphide, chloroform, benzol, etc. The principal impurities of phosphorus are arsenic and sulphur. To detect these one part of phosphorus is dissolved at gentle heat in 14 parts of nitric acid of 40%, spec. gr. 1.251; after solution the liquid is evaporated to expel nitrous fumes and sur-

plus of nitric acid. The solution should now contain pure ortho-phosphoric acid, which may be tested as directed on page 17. No yellow precipitate of arsenic should be produced by protracted passing of H_2S. *Gutzeit's* modification of *Marsh's test*, in which hydrogen is produced by pure zinc and pure dilute acid in a long test tube, covered by a cap of filter paper moistened with a drop of conc. solution of silver nitrate, must, after addition of the phosphoric acid solution, show no sign of arsenic during half-an-hour, by a yellow color of the silver spot turning to black by moistening. In the dilute solution of phosphoric acid barium chloride should produce no precipitate.

Exposure to light and air changes the external portion to an opaque white, while the interior turns yellow or red.

Red phosphorus is insoluble in CS_2, more stable in air, and requires 260° C. for ignition. The tests for purity applied after oxidation are the same as for the ordinary variety.

PREPARATION. It will hardly be attempted to manufacture phosphorus from bone ashes on the small scale. To convert it into the thin pencils used in gas analysis a sufficient amount of phosphorus is melted under water in a capacious test tube to form a layer of 6 Cm. in depth. Into this a narrow glass tube, slightly conical, is immersed with the wider end down, the top is closed with the finger, and tube and contents transferred to a beaker of cold water. The melted phosphorus shrinks in solidifying and drops into the beaker in the shape of a thin pencil. The product must be carefully preserved under water in a bottle surrounded by a metallic box.

Red phosphorus is made by heating the ordinary phosphorus in a close tube, freed from oxygen, to 300° C. It generally contains some unchanged phosphorus of the ordinary variety, which may be dissolved out by carbon disulphide.

PHOSPHORUS PENTOXIDE, P_2O_5.

USES. Phosphorus pentoxide, or anhydrous phosphoric acid, on account of its great affinity for water, is employed for dehydration of bodies containing water, or for decomposing those which contain hydrogen and oxygen. It serves to concentrate acids by withdrawal of water, and is, therefore, useful as an addition to sulphuric acid used in *Kjeldahl's* process for converting the nitrogen of organic bodies into ammonium salts.

TESTS. Phosphorus pentoxide forms white, amorphous flocculi, which, at a high temperature, sublime unchanged and without residue. From air it attracts moisture and liquefies. Dropped into water it hisses and dissolves into meta-phosphoric acid. Its

solution is tested for arsenic like that of phosphorus.

PREPARATION. By burning phosphorus in a suitable apparatus in dry air or oxygen.

PLATINUM AND ITS COMPOUNDS.

PLATINUM, Pt.

USES. In the state of wire or foil, or wrought into various shaped vessels, the metal, on account of its high fusing point (near 2,600° C.), serves as a support in many operations requiring high temperature, fluxions, blowpipe work, etc. Its insolubility in most acids renders it most valuable as material for vessels in which hydrofluoric acid, concentrated sulphuric acid, etc., are distilled. In a state of fine subdivision, as platinum-black or sponge or platinized asbestus (see page 47), it condenses up to 200 volumes of oxygen, and thereby serves to unite this with hydrogen or vapors containing it. In nitro-hydrochloric acid it dissolves, and from the chloride thus obtained other preparations are made.

By the aid of zinc platinum foil serves to recognize antimony, which, when dropped upon the foil in acid solution, is reduced by the zinc to black metallic antimony, which closely adheres to the platinum foil. $Pt = 194.415$.

Cautions in using platinum vessels. Many substances, when brought in contact with metallic platinum, are capable of injuring it, either by alloying with it at high temperature or by corroding or dissolving it. Hence, neither chlorine nor compounds capable of evolving it must be treated in platinum vessels. Caustic alkalies, especially lithium and mixtures from which they may result, are liable to corrode platinum vessels in which they are fused, unless air can be absolutely excluded from them (it is supposed that a peroxide forms, to which the corrosion is due). Alkaline nitrates, sulphides, phosphides, cyanides, metals or metallic sulphides, oxides or organic salts, from which metals may be easily reduced, are likewise injurious. When it is necessary to heat a platinum crucible in a charcoal or coke furnace, it must be encased in calcined magnesia, contained in a Hessian crucible, to avoid direct contact with the fuel. Over a gas or alcohol lamp it may be heated in direct contact with the flame, provided it be supported on a triangle of platinum wire, so as to avoid contact with other metallic support at high heat. To clean platinum crucibles or capsules from material closely adhering after fluxions, etc., scouring with round sea sand, or fusing in them borax or acid potassium sulphate, may become necessary. They should be occa-

sionally burnished to prevent scaling and formation of fissures; for this purpose a wooden block, fitting accurately into the vessel, is very useful, as it gives a firm support and enables the restoration of indented parts into perfect shape.

PREPARATION of platinum in a fine state of subdivision. That of platinum asbestus, by means of reduction of platinic chloride by a salt of formic acid, is already described on pages 46 and 47.

Platinum black is made by reducing platinum chloride, either by metallic zinc, etc., or better, by reducing platinum chloride, dissolved in glycerin by boiling with sodium hydrate, washing thoroughly and drying.

Platinum sponge is made by precipitating platinic chloride by ammonium chloride, forming the yellow double salt, $Pt\,Cl_4 . 2\,N\,H_4\,Cl$, which is washed and ignited, and thus leaves the metal as a gray, coherent mass of somewhat less fineness of subdivision than platinum black.

PLATINIC CHLORIDE, $Pt\,Cl_4$, and CHLORO-PLATINIC ACID, $H_2\,Pt\,Cl_6 + 6\,H_2\,O$.

USES. Under the name of platinum chloride both of the above preparations are used indiscriminately. The commercial article, dry or in solution, generally contains chloro-platinic (or platino-hydrochloric) acid, which differs from the neutral $Pt\,Cl_4$ by an additional $2\,H\,Cl + 6\,H_2\,O$. They serve for the detection and quantitative determination of potassium, rubidium, cæsium, ammonium and thallium, which are precipitated as chloro-platinates (usually called double salts), insoluble in alcohol, while the sodium salt is very soluble, but may be recognized by its crystals under the microscope. They are also used for the detection and quantitative determination of many alkaloids, which are precipitated as insoluble chloro-platinates, while others (atropine, aconitine, veratrine) are soluble. A few drops of the solution added to pure zinc, cadmium, etc., render them more soluble in acids by the establishment of galvanic action. An empirical volumetric solution of sodium chloro-platinate in dilute alcohol is used for titration of potassium salts; 12 to 15 gr. of the sodium salt are dissolved in 100 Cc. of 50% alcohol, and its effective titre ascertained by pure potassium nitrate. It is then used for addition to specimens to be tested, the potassium chloro-platinate separated, and in the filtrate the platinum is first precipitated by zinc and then the residue of chlorine determined by silver nitrate. The difference in the chlorine of the chloro-platinate added and that of the residue left after precipitating the potassium salt, readily admits of the calculation

of potassium present (Dubernard). $Pt\ Cl_4 = 335.895$; $H_2\ Pt\ Cl_6 = 408.635$; $H_2\ Pt\ Cl_6 + 6\ H_2O = 516.395$.

TESTS. $Pt\ Cl_4$ forms brown deliquescent masses, soluble in 8 parts of absolute alcohol. It is capable of crystallizing with $5\ H_2O$ in red crystals; at 100° C. these lose 1 mol. water and turn brown. From its solution in hydrochloric acid red needles of chloro-platinic acid crystallize with 6 mol. water. These, by heating, lose, first, water and hydrochloric acid, then chlorine, forming at 225° dark-brown platinous chloride. Protracted ignition dissipates all chlorine and leaves metallic platinum, which, if the salt was pure, should yield nothing soluble to nitric acid. Salt, containing platinous chloride, $Pt\ Cl_2$ (by over-heating in drying), leaves a greenish-brown residue when dissolved in alcohol.

PREPARATION. Metallic platinum, cut into small chips, is first boiled in nitric acid to remove any substance soluble in it; it is then washed, dried and boiled in hydrochloric acid. After again washing and drying, 1 part is placed into a flask with 7 parts of hydrochloric acid of spec. gr. 1.16, and heated to 80° C.; 1½ parts of nitric acid are then added in small portions, 10 or 12 drops at a time, and time given for the reaction to be completed, until all but a very small residue is dissolved. The solution is filtered into a porcelain dish and evaporated at 100° C. until the residue solidifies on cooling. To decompose a small rest of nitric acid yet present, a small amount of hydrochloric acid is added and the solution again evaporated; it is then redissolved in some water and again evaporated, as long as acid vapors escape. The residue is then dissolved in enough water to make the solution contain 5% of metallic platinum (*Post*).

POTASSIUM AND ITS COMPOUNDS.

NOTE. In a great many analytical operations it is immaterial whether the salts of potassium or those of sodium with the same acid are employed, making in quantity due allowance for the difference in atomic weights. Hence, the description of uses, tests and preparation of potassium compounds, to a great extent, apply to those of sodium as well, and need not there be fully repeated. It is only when metallic bases are to be removed or detected without introducing sodium, or when acids are to be detected which, as tartaric acid, form difficultly soluble salts with potassium, but not with sodium, that sodium compounds can not be substituted for those of potassium.

POTASSIUM, K.

USES. Metallic potassium serves to detect nitrogen in organic substances by uniting, at high temperature, with it and carbon to form potassium cyanide (*Lassaigne*). This method does not apply

to di-azo-compounds, whose nitrogen volatilizes before the metal can act (*Graebe*). Potassium may also be employed, either alone or as amalgam, for the reduction of many compounds, but for this the cheaper sodium is generally preferred. In absolute alcohol it dissolves, while hydrogen escapes, forming *potassium ethylate*, $K.C_2H_5O$, which is sometimes used for the reduction of nitro-compounds (*Maumene*). K = 39.019.

TESTS. Metallic potassium is of silver-white lustre, of spec. gr. 0.86; it melts at 62.5° C., and between 719° to 731° is converted into green vapor. It rapidly attracts oxygen from air, water, ice, etc., and must, therefore, be preserved under petroleum naphtha. Thrown on water it ignites and forms hydrate, which dissolves. In air it burns with violet flame, visible through blue glass or indigo solution. This flame, observed with the spectroscope, should show the pure spectrum, free from sodium and other lines. For analytical purposes the metal of commerce is sufficiently pure.

PREPARATION. On the large scale, by heating to bright redness, in a suitable iron distilling apparatus, a mixture of potassium carbonate and charcoal, such as is obtained by charring cream of tartar. Great caution is necessary to guard against explosions. The metal may be redistilled in a current of dry hydrogen.

POTASSIUM ACETATE, $K.C_2H_3O_2$.

USES. For the detection and separation of tartaric acid in wine, etc. Also, instead of sodium acetate in the Kakodyl test for arsenic (*Cadet*). In this, by infusing arsenic trioxide with an acetate the malodorous dimethyl arsine is formed. Also for the various other reactions instead of sodium acetate, when the introduction of sodium is to be avoided. Mol. W. = 97.887.

TESTS. Potassium acetate is a very deliquescent, colorless salt, soluble at 15° C. in 0.4 parts of water and in 4 parts of alcohol. When brought in contact with concentrated sulphuric acid it does not color it brown, unless it contains organic impurities derived from tarry matters of pyroligneous acetic acid. Neither hydrogen sulphide, ammonium sulphide, sodium carbonate, potassium ferrocyanide, silver nitrate nor barium chloride should render the solution turbid or produce in it any color. No effervescence should occur with acetic acid. After addition of an excess of hydrochloric acid and evaporation to dryness, it must redissolve in water without residue. The flame colored by it should show no sodium line in the spectroscope.

PREPARATION. Neutralize pure potassium di-carbonate (or carbonate with pure acetic acid), evaporate and crystallize.

POTASSIUM BROMATE, $K\,Br\,O_3$.

USES. To make solution of bromine for the volumetric determination of phenol according to *Koppeschaar's* method. As bromine is too volatile to keep titre for any length of time, the solution is prepared only as needed by mixing equal volumes of a solution containing 0.01 of the molecular weight of $K\,Br\,O_3$, expressed in grammes, = 1.668 gr. in 500 Cc. of water, and of a solution containing 0.05 Mol. W. of K Br = 5.939 gr. in 500 Cc. The litre of liquid thus mixed contains 4.786 gr. of bromine, which is liberated by a sufficient amount of hydrochloric or sulphuric acid, and is capable of converting 0.01 Mol. W. = 0.938 gr. of phenol into tribrom-phenol. When 50 Cc. of each solution are mixed and added to 0.938 gr. of pure phenol and 5 Cc. of acid, the whole amount is converted and no residue of bromine left, but if the phenol contained impurities then only part of the 100 Cc. of solution expends its bromine, and the residue is measured by adding K I and starch, and determining the liberated iodine by deci-normal sodium hyposulphite. The process may be so modified, that the bromine solution is added to the phenol and acid from a burette until all phenol is precipitated and the percentage read off directly, paper moistened with starch and zinc iodide being used as indicator. Other modifications are used. Thus, *Allen* makes the mixture of the salts by saturating a hot solution of alkaline hydrate (potassium or sodium) with bromine, evaporating to dryness and adjusting the titre of the solution by pure phenol. Sodium salts, in proper proportion, are frequently used in the place of those of potassium. $K\,Br\,O_3$ = 166.667 (K. Br = 118.787; $Na\,Br\,O_3$ =150.646; Na Br = 102.766).

TESTS. Potassium bromate crystallizes in the hexagonal system, forming rhombohedra closely resembling regular cubes. At 15° it requires about 18 parts of water for solution; at 100° C. only 2.1 parts. At 350° C. it melts, and a higher heat gives off all its oxygen and becomes K Br. It is best tested for purity by titration with silver nitrate. When 1.66667 gr. are dissolved in water it requires 100 Cc. of deci-normal silver nitrate to precipitate them as silver bromate. Or if the same quantity of salt be first deprived of oxygen, by heating in a platinum crucible, the solution requires 100 Cc. of deci-normal silver nitrate to form silver bromide, if the salt was pure.

Or else 1.66667 gr. are dissolved in water, 2 gr K I, starch and a slight excess of hydrochloric acid are added and then titrated with deci-normal sodium hyposulphite (thiosulphate). Pure salt requires exactly 100 Cc.

PREPARATION. Four parts of potassium carbonate are dissolved in 8 parts of water and 1 part of bromine added; chlorine gas is then passed through the mixture. Crystals of potassium bromate separate and are recrystallized from boiling water.

POTASSIUM BROMIDE, K Br.

USES. For the preparation of bromine solution (see bromate); also of hydrobromic acid; also for the detection of small quantities of copper (*Endemann and Prochazka*); a crystal of potassium bromide is thrown into the solution and then conc. sulphuric acid added, if copper be present, the crystal surrounds itself by deep-red cupric bromide. K Br = 118.787.

TESTS. Pure potassium bromide crystallizes in colorless or white cubes. At 20° C. it dissolves in 1.55 parts of water, at 100° in 0.98. Moist red litmus paper must not be turned blue by it. Addition of dilute $H_2 S O_4$ must produce neither effervescence nor yellow color. When ferric chloride or chlorine water are added to its solution, starch added to it must not be colored blue, nor chloroform shaken with it assume a violet color. When distilled with potassium dichromate and sulphuric acid, no chlorochromic acid must pass into the distillate, as shown by its remaining colorless when saturated by ammonia. To the flame it must not communicate the yellow color of sodium. The absence of other metals is shown as in potassium acetate. 1.1879 gr. must require exactly 100 Cc. of deci-normal silver nitrate for precipitation.

PREPARATION. On the large scale, either by double decomposition of ferrous bromide and potassium carbonate, or by adding bromine to potassium hydrate, decomposing by charcoal and heat the bromate formed and crystallizing. Either process may be used on the small scale, or pure hydrobromic acid may be neutralized by pure potassium carbonate and crystallized.

POTASSIUM CARBONATE.

a. NEUTRAL POTASSIUM CARBONATE, $K_2 C O_3$.

USES. For the precipitation of many metallic bases, some of which may be recognized by characteristic colors. For neutralization of acids. Mixed with sodium carbonate it serves as a flux for the decomposition of insoluble silicates, titanates, barium salts, etc., the mixture fusing at a lower temperature than either of the constituents unmixed. Also in blowpipe operations, instead of sodium carbonate, to detect sulphates by the hepar test, to reduce metals, etc. Also in various tests for glucose (Boettger's,

Mulder's etc.) to render liquid alkaline. Also for the preparation of various compounds of potassium and as volumetric solution in acidimetry. $K_2CO_3 = 137.892$.

TESTS. Potassium carbonate is rarely sold in crystals, $(K_2CO_3)_2 + 3H_2O$; generally as a coarse, white powder, very deliquescent, soluble in 1 part of cold and ⅜ parts of hot water. Its solution must not yield a precipitate with ammonium carbonate or sulphide. After slightly supersaturating with acetic acid it must give no precipitate with H_2S, $BaCl_2$ or $AgNO_3$. The absence of arsenic must be proven by *Fleitmann's* test (page 14) or *Gutzeit's* (see H Cl, page 8; Fe S, page 117; Mg, page 124; $AgNO_3$; Zn). With silver nitrate the solution must give a pure white precipitate, which neither darkens by gentle heating nor leaves any residue on addition of an excess of nitric acid. With di-phenyl-amine or pyrogallol and sulphuric acid it must not show the color of nitric acid. After acidulating with H Cl and evaporating to dryness the residue must completely redissolve in water (abs. of silica). Ammonium molybdate must not give a precipitate in the solution acidulated by nitric acid. When the solution is gently heated with a few drops of ferric chloride and ferrous sulphate solution it must not yield a blue color on acidulation with hydrochloric acid. The flame color must be violet, showing absence of sodium.

PREPARATION. The purest salt is prepared from cream of tartar, purified first by repeated recrystallization, and then by digesting for some hours on a water bath with an equal weight of water containing 3% of H Cl. The mass is then placed upon a funnel, closed with a light prop of asbestus, filter paper or cotton, and washed by covering it with a disk of filter paper, upon which cold water is poured repeatedly, in small portions, until silver nitrate fails to show H Cl in the wash water. The purified cream of tartar is then dried and incinerated in a clean, iron dish, either alone or after mixing with half its weight of pure potassium nitrate. The charred mass is leached out with water, filtered and evaporated until it begins to show a solid crust. It is then cooled and the crystals of potassium carbonate are drained on a funnel, rinsed with a little water and then dried. An article pure enough for most purposes is obtained by recrystallizing commercial potassium di-carbonate (bi-carbonate), washing the crystals upon a funnel until after acidulation with nitric acid the wash water is no longer rendered turbid by barium or silver nitrate, and then heating them above 106° C. up to 190° in a silver or platinum dish, until half of the carbonic acid is expelled and pure neutral carbonate left. The solution is generally made to contain 10 %. For fluxing, 5.3 parts of anhydrous

sodium carbonate are thoroughly mixed with 6.9 parts dry potassium carbonate.

Normal solution contains 68.946 gr. in 1 litre, but can not be made by direct weighing, unless the salt is ignited just before weighing and not permitted to attract moisture. It is made by adjusting by dilution the titre of a stronger solution, so as to correspond with normal acid solution, methyl orange being used as indicator.

b. ACID POTASSIUM CARBONATE, $KHCO_3$.

(*Di or Bicarbonate.*)

USES. For the preparation of *Soldaini's* reagent for glucose (see page 93); for introduction of carbonic acid into combustion tubes, in *Dumas'* method for determining nitrogen in organic compounds, by heating the salt to a temperature between 106° to 190° C., when it parts with CO_2 and H_2O, while K_2CO_3 is left behind ($2KHCO_3 = K_2CO_3 + CO_2 + H_2O$). Also for separation of the quinine group of alkaloids, which from *acid* solutions are precipitated by potassium acid carbonate, from the strychnine group, which are not thus precipitated. Also for the preparation of pure potassium carbonate and other salts. $KHCO_3 = 99.873$.

TESTS. Potassium dicarbonate crystallizes in colorless mono. clinic prisms, soluble at 15° in 4 parts of water. When entirely free from neutral carbonate it does not attract moisture from the air, nor does its solution in 20 parts of cold water precipitate magnesium sulphate. For the preparation of pure potassium compounds it must stand the tests as described for potassium carbonate; for most puposes the commercial salt is sufficiently pure.

PREPARATION. Potassium carbonate is dissolved in about 3 parts of water, and a slow current of carbonic acid gas is passed through it for several days. Large crystals of dicarbonate form, and are drained and purified as directed for the preparation of potassium carbonate, page 154. Or pure, dry potassium carbonate, made from cream of tartar, is exposed for some time to an atmosphere of carbon dioxide. It is then dissolved and crystallized, if necessary, taking, however, great care to use no heat, as in solution the dicarbonate loses CO_2, and is converted into the neutral salt much below the boiling point.

POTASSIUM CHLORATE, $KClO_3$.

USES. For preparing oxygen gas (page 139). Potassium chlorate melts at 359° C., and at a somewhat higher temperature is decomposed into oxygen, potassium chloride and perchlorate, which, at a

still higher heat, also loses its oxygen and is converted into chloride. When about 5% of $Mn O_2$, $Pb O_2$ or $Cu O$ are mixed with the chlorate it yields its oxygen at from 260° to 270° C. It is also used in forensic analysis together with hydrochloric acid to destroy organic matters, so as to prepare the way for examination for metallic poisons (*Fresenius and Babo*). $K Cl O_3 = 122.269$.

TESTS. Potassium chlorate crystallizes in the monoclinic (monosymmetric) system, mostly in colorless, transparent tables. It is soluble in 16.7 parts of water at 15° C. and in 1.75 parts at 100°. Its dilute solution is neutral to test papers, and must not give precipitates with hydrogen sulphide, barium chloride, silver nitrate, ammonium oxalate or potassium ferrocyanide. After ignition on platinum foil the residue must be completely soluble in water, of neutral reaction and give no precipitate with mercuric chloride. It must show no trace of arsenic by the most sensitive tests.

PREPARATION. On the large scale, by *Graham's* process of saturating with chlorine gas a moist mixture of 1 molec. potassium carbonate with 8 mol. of calcium hydrate, leaching out with water, filtering and crystallizing. Or from 1 mol. potassium chloride and 3 mol. calcium hydrate and chlorine. On a small scale it may be made by passing pure chlorine through a hot concentrated solution of pure potassium hydrate or carbonate. The crystals separate and are purified by recrystallization.

POTASSIUM CHROMATE, $K_2 Cr O_4$.

USES. For the precipitation of barium and strontium and their separation, as strontium chromate is soluble, barium insoluble in acetic acid (*J. Lawrence Smith*). For detection of silver, lead and mercurous salts, which give precipitates of characteristic color. As a test for barium dioxide, etc., by production of blue color. As indicator in the titration of chlorides, etc., by silver nitrate (*Mohr*). In deci and centi-normal solution, containing 9.6943 gr. and 0.969 gr. $K_2 Cr O_4$ in the litre, for adjusting the titre of volumetric solution of iodine (*L. Crismer*), and of sodium hyposulphite (Zulkowsky). $K_2 Cr O_4 = 193.887$.

TESTS. Potassium chromate crystallizes in yellow, rhombic pyramids, isomorphous with $K_2 S O_4$, soluble at 15° in 1.65 parts of water. At high heat it melts without decomposition. Metallic impurities are detected in similar manner as in other potassium salts. Of other acids it is most likely to contain sulphuric and hydrochloric. Its solution in dilute hydrochloric acid must give no precipitate with barium chloride. The precipitate produced by silver nitrate in its aqueous solution must completely redissolve in nitric acid.

PREPARATION. Fifteen parts of potassium dichromate are dissolved in water and 7 parts of dry potassium carbonate added. The solution is concentrated by evaporation and set aside to crystallize. Any dichromate remaining undecomposed is deposited first; as soon as only yellow crystals begin to form the motherlye is poured off, and from it the neutral chromate is obtained and purified by recrystallization.

POTASSIUM DICHROMATE, $K_2 Cr_2 O_7$.

USES. Potassium dichromate (bichromate or acid chromate) is used for separation of barium from strontium, as in aqueous or acetic acid solution it forms a precipitate with barium, but not with strontium (*J. Lawrence Smith*). Also for detecting lead, silver and mercurous salts; also hydrogen dioxide and dioxides producing it by the blue color of perchromic acid, soluble in ether. Also as a test for alkaloids, either as *Luchini's* reagent, a saturated solution in hot concentrated sulphuric acid, which produces characteristic appearances with several alkaloids and glucosides, or in saturated aqueous solution, or in the dry state with concentrated sulphuric acid. By the latter method strychnine gives the characteristic series of color changes from deep blue through shades of violet and purple to a final yellowish-red. Aniline with similar treatment produces a blue color, which soon disappears. Atropine, heated with dichromate and sulphuric acid, emits the odor of bitter almonds; amyl alcohol is converted into valerianic acid; malates give the odor of fresh apples (*Papasogli and Poli*). In aqueous solution it produces with benzidine a deep blue precipitate, insoluble in most solvents (*Julius*). It is also used for the oxidation of carbon and its determination as $C O_2$ in the *McCreath-Ullgren* method of iron analysis (see cupri-tetrammonium chloride, page 100), and for estimation of cellulose (*Cross and Bevan*); great care must be taken to avoid the inaccuracies arising from imperfect oxidation to C O instead of $C O_2$. In microscopical examinations it serves not only for hardening tissues, but also as a reagent for differentiating various tannic acids, etc. (*Sanic*, *Nickel*). In organic analysis it also serves to oxidize sulphur. In volumetric analysis a *deci-normal* solution containing 14.6888 gr. $K_2 Cr_2 O_7$ in 1 litre is used to convert 16.7734 gr. of iron from ferrous into ferric salt, potassium ferricyanide serving as indicator by spotting (*Penny*, *Schabus*). Sometimes the solution is made with 4.896 gr. in 1 litre, being $\frac{1}{3}$ of the deci-normal strength, so that if 5.591 gr. of iron be weighed as a specimen each Cc. corresponds to 1 % of Fe. *Centi-Normal* solution is also used. *Normal* solution, containing

146.888 gr. in 1 litre, is used in alkalimetry with phenol-phthalein as indicator (*Richter*), having the same value as equal volumes of normal sulphuric, oxalic and other acids. $K_2 Cr_2 O_7 = 293.776$.

TESTS. Pure potassium dichromate forms large, red triclinic (asymmetric) prisms or tables, soluble in 10 parts of water at 15°, in 1.1 parts at 100° C. At a low red heat it fuses; at white heat it is decomposed into oxygen, chromic oxide and yellow neutral chromate. It should conform to the same tests for purity as the neutral chromate, and 14.689 gr. should require exactly 100 Cc. of normal potassium hydrate for neutralization.

PREPARATION. Commercial salt is dissolved in 10 parts of hot water, and if sulphates are found present they are removed by adding a little baryta water, mixing thoroughly and setting aside for some hours before filtering. For the removal of chlorides, freshly precipitated oxide of silver is used in similar manner. The filtered solution is then concentrated and very small crystals obtained, these are drained, washed and recrystallized. Before weighing out for making volumetric solutions the salt is fused to remove moisture accidentally enclosed. For ordinary qualitative work a 10% (saturated) solution is used. A special solution for detection of strychnine is made by dissolving 0.01 gr. potassium dichromate in 5 Cc. water, and adding 15 gr. (8.15 Cc.) sulphuric acid of spec. gr. 1.84. After cooling, the solution of these proportions gives better results than others by the greater permanence of the blue color (*Flueckiger*).

POTASSIUM CYANIDE, K C N.

USES. Dry potassium cyanide is used at high temperature as an active reducent of metals not so easily reduced by other means, especially of tin, antimony, arsenic, etc., from their oxides and sulphides. In blow pipe analysis it serves, mixed with sodium carbonate, for many reductions on charcoal. Also, to detect sulphur, sulphides and sulphates by the production of rhodanate (sulphocyanate). In solution it serves for the precipitation of metals, some of which redissolve, forming double cyanides, while others do not. Of the soluble ones, some are again precipitated by acids (Ni, Zn, Mn, Cd, Cu, etc.) as cyanides, or as hydrates by addition of bromine or chlorine (nickel), while iron and cobalt are, by boiling with a surplus of potassium cyanide (in presence of some free hydrocyanic acid), converted into compound cyanides, which are not precipitated either by acids, bromine or chlorine. Upon this behavior depends the application of K C N for the separation of cobalt from nickel. Potassium cyanide dissolves cupric sul-

phide, but leaves cadmium sulphide undissolved, thus permitting the separation of these metals. From a solution of their double cyanides, ammonium sulphide precipitates zinc, but not nickel, and is therefore used in *Woehler's* method for their separation. In electrolytic analysis potassium cyanide serves to prepare solution of gold, etc. It is also used for the titration of copper ores by *Parkes'* method, the copper being dissolved in ammonia and ammonium carbonate (*Fleck*, *Jeller*). It also serves to detect picric acid by the red color of the isopurpuric acid formed. Also to distinguish gallic acid, which it colors red, from tannic acid, which is not colored (*Young*). $KCN = 65.014$.

TESTS. When crystallized by fusion and slow cooling or from alcoholic solution, potassium forms regular octohedra or cubes. It is generally sold in fused masses or granules, easily soluble in water, slightly in absolute alcohol. The aqueous solution rapidly decomposes, forming ammonia and potassium formate. If fused with access of air it always contains cyanate, and the commercial article is seldom free from this and carbonate. It may, however, be used for many purposes, if free from sulphur and silicic acid. It must yield with lead acetate a pure white precipitate, and with ferric chloride must not give a red solution. After acidulation with hydrochloric acid and evaporation to dryness, the residue must completely dissolve in water. For separation of metals a pure salt must be employed, which, in addition to above tests, and those directed to show absence of metallic impurities in all potassium salts, must show especially absence of chloride, cyanate and carbonate. Hence, the precipitate occasioned in its solution by silver nitrate must be completely dissolved in nitric acid. Cyanate is discovered by heating the aqueous solution and then adding potassium hydrate, when ammonia will be evolved, derived from decomposition of the cyanate. Carbonate is shown by the gas liberated by dilute hydrochloric acid, rendering limewater turbid.

PREPARATION. On the larger scale potassium cyanide is made, according to Liebig's method, by drying yellow potassium ferrocyanide, free from sulphate, by gentle heat, so as to render it anhydrous, mixing 8 parts with 3 parts of dry potassium carbonate, and fusing the mixture at a low red heat in an iron vessel, well covered to prevent access of air, until the yellow color has entirely disappeared, and pouring the fused mass, after subsidence of the finely divided iron, into suitable vessels. To purify this, the ordinary commercial salt, it is dissolved in 50% alcohol, filtered and obtained dry by evaporation. An absolutely pure product for separation of metals is obtained by passing the vapors of hydrocyanic

acid, as they come from the retort into an alcoholic solution of pure potassium hydrate. This is evaporated and kept in the dry state, as the solution rapidly decomposes, even at ordinary temperatures.

POTASSIUM SILVER CYANIDE, $Ag\,C\,N\,.\,K\,C\,N$, is occasionally used to precipitate quinine, quinidine, cinchonine, cinchonidine and other alkaloids. As it very rapidly spoils, the solution is made when needed by adding to a concentrated solution of silver nitrate one of potassium cyanide until the silver cyanide at first precipitated is completely redissolved.

POTASSIUM CUPRIC CYANIDE, $Cu\,(C\,N)_2\,.\,2\,K\,C\,N$, has been used for a similar purpose as the silver salt, but is less stisfactory; it is made, like the preceding, only when needed from cupric sulphate and potassium cyanide.

POTASSIUM PLATINUM CYANIDE, $Pt(C\,N)_2 + 2\,K\,C\,N + 3\,H_2\,O$, is sometimes used for the precipitation of the salts of alkaloids as platino-cyanides; free alkaloids are not precipitated (*Schwarzenbach*, *Delffs*). It is made by heating equal parts of spongy platinum and potassium ferro-cyanide to a low red heat, extracting the fused mass with water and crystallizing. It forms long prisms, blue in reflected, yellow in transmitted light.

POTASSIUM FERROCYANIDE, $K_8\,Fe_2''\,(C\,N)_{12} + 6\,H_2\,O$.

USES. Potassium ferrocyanide, or yellow prussiate, forms precipitates with many metals, some easily identified by characteristic colors: white, Ag, Al, Bi, Ca, Cd, Hg, Mn, Pb, Sb, Sn; yellowish-white, Mg; greenish-white, Ni; green, changing to gray, Co; white, changing to blue ferrous; dark blue ferric; red-brown Cu, uranic; brown uranous, Mo. Some of these are decomposed by alkalies, others are not. Hence, a method of separating iron from manganese by adding citric acid and ammonia to their mixed ferrocyanides; ferric salt is decomposed by the ammonia and dissolves in the citrate; manganese remains unaffected (*Blum*). In gallium salts the precipitate only falls in presence of excess of H Cl (*Lecocq de Boisbaudran*). Sometimes a volumetric solution is used for titration of zinc (*Galetti*). $K_8\,Fe_2''\,(C\,N)_{12} + 6\,H_2\,O = 843.678$.

TESTS. Potassium ferrocyanide crystallizes in transparent yellow monoclinic tables, whose angles so nearly approach the square (89° 27′) that, until recently, they were assigned to the quadratic system (*Wyrouboff*, *Groth*). At 15° it dissolves in 4 parts, at 100° in 2 parts of water; insoluble in alcohol. Sunlight gradually decomposes the solution, depositing prussian blue. The water of crystallization

is lost below 100°; fusion converts it into potassium cyanide, iron carbide and nitrogen: $K_8 Fe_2'' (C N)_{12} = 8 K C N + 2 Fe C_2 + 2 N_2$. For most purposes of analysis the recrystallized commercial salt is sufficiently pure; absence of sulphates is proven by barium chloride, whose precipitate must redissolve in hydrochloric acid or in much boiling water.

PREPARATION. The commercial salt is purified by adding to the solution sufficient baryta water to precipitate sulphates, filtering and repeatedly crystallizing. One part is dissolved in 12 parts of water, and the solution, as well as the dry salt, preserved in dark bottles.

POTASSIUM FERRICYANIDE, $K_6 Fe'''_2 (C N)_{12}$.

USES. Potassium ferricyanide, or red prussiate, is by light and other reducents easily converted into the yellow salt; hence, it serves, especially in alkaline solution, to oxidize alcohol, oxalic acid, carbohydrates, indigo and other organic substances; also phosphorus to phosphoric, sulphur to sulphuric acid. With nitrogen dioxide it forms nitric acid, being at the same time converted into nitro prusside. It is mostly used to detect ferrous salts by precipitation of Turnbull's blue, manganese by a brown, nickel by a brownish-yellow, cobalt by a red-brown precipitate. If to the cobalt solution ammonium tartrate or chloride and then free ammonia is added and then ferricyanide a deep-red solution results, capable of detecting traces of cobalt in presence of nickel (*Skey, Gentl*). In conjunction with sulphuric acid ferricyanide serves to detect aniline by a blue to purple color (*Letheby*). Its solution mixed with ferric chloride forms a brown solution of *ferric ferricyanide*, which, by reduction to prussian blue, serves to detect morphine and other alkaloids and reducing ptomaines. $K_6 F_2''' (C N)_{12} = 657.880$.

TESTS. Potassium ferricyanide forms deep-red, rhombic crystals of long, tapering columns, with almost a square base. It is soluble in 2.6 parts of water at 15° C.; in 1.3 at 100°. Its solution is rapidly decomposed by light, while fresh it must give a clear brown solution with ferric chloride.

PREPARATION. Five parts of the yellow ferro-cyanide are dissolved in 50 parts of water, thoroughly mixed with 1 part of bromine and set aside in a dark place (or the solution is fully saturated with chlorine gas) until a drop of the solution no longer produces a blue color with ferric chloride. The solution is then evaporated to about one-fifth of its volume and set aside to crystallize. The crystals are drained and purified by recrystallization. All

operations and the preservation must strictly exclude light. Solution is made only when needed.

POTASSIUM FLUORIDE, K F, and potassium hydrogen fluoride are sometimes used instead of the ammonium salt in the analysis of silicates, borates, titanates, etc. Tests and preparation are similar to ammonium salt (see page 34).

POTASSIUM HYDRATE, K O H.

USES. For neutralization of acids and for their titration by means of volumetric standard solutions, which are preferable to sodium hydrate on account of less liability of corrosion of burettes and to ammonia on account of greater stability of titre. For precipitation of insoluble metallic hydrates from the solutions of their salts. Some of these are soluble in excess of the reagents, as aluminium, beryllium, chromium, zinc, lead, and may, therefore, be separated from the insoluble ones, as iron, manganese, cadmium, bismuth, etc. By boiling the solution chromium and beryllium are again precipitated, but not aluminium, zinc or lead. Beryllium may thus be separated from aluminium, but only when the solution of K O H is so diluted that it contains 0.1 % of the mixed hydrates, otherwise the precipitate of beryllium hydrate carries with it some aluminium (*Zimmermann*). In ultimate organic analysis K O H serves to determine the quantity of $C\,O_2$, which is absorbed either by solution of potassium hydrate contained in Liebig's bulbs, or their modification, or by solid hydrate in suitable tubes. Also for making *Moore's* (*Heller's*) test for glucose, whose solution it colors brown, slowly in the cold, rapidly when heated. Also as addition in other glucose tests by cupric, bismuth, mercuric and other salts, picric acid, etc. Also for giving color reactions with some alkaloids by fusing them with dry K O H, grass green with quinine and quinidine, blue-green with cinchonine and cinchonidine, greenish-yellow, changing to red with cocaine (*Lenz*). Also in microscopic work for clearing up and corrosion of tissues, separating starch from the epidermis of grains in flour examinations; for coloring lignin yellow (woodpulp in paper); for saponification of fats, etc. Also for preparation of a stable solution of starch (Mueller). K O H = 55.979.

TESTS. Potassium hydrate is usually sold as a white, fused mass, often molded into thin pencils, and of different degrees of purity. For filling potash bulbs and tubes for absorption of $C\,O_2$ a moderate degree of purity suffices. Neither is absolute purity required for volumetric solution to determine the percentage of acids, as the solution is standardized by normal acids, nor for de-

tection of glucose, for fusion with alkaloids or for microscopic work. But for separation of metals, for determination of sulphur in organic compounds, potassium hydrate must be pure. Small traces of sodium hydrate are objectionable only in special cases.

Pure potassium hydrate dissolves without residue at 15° C. in 0.47 parts of water and in 2 parts of alcohol; in either case no deposit must show itself after dilution with the solvent and standing for some hours. After acidulation with acetic acid no precipitate must be produced by H_2S; nor after such acidulation and subsequent addition of a slight excess of ammonia must any precipitation be produced by addition of ammonium sulphide or oxalate, nor by simply simply heating to 100° for half an hour, with occasional replacing of the evaporated ammonia, and setting aside to cool. To detect traces of impurities, several grammes of KOH must be examined. After acidulation of the KOH solution with nitric acid neither ammonium molybdate, nor barium chloride, nor silver nitrate must occasion any turbidity. To detect traces of carbonate in the hydrate, a solution of 15% is made and added to a mixture of 10 Cc. saturated solution of calcium sulphate with 5 Cc. of water; 0.2% of carbonate produced a decided precipitate of calcium carbonate (*Koster*).

After acidulation with HCl and evaporation to dryness no insoluble residue must be left. After acidulation with sulphuric acid and addition of a few crystals of pure pyrogallol, the solution of potassium hydrate must not show a brown or yellow zone of contact when stratified over concentrated H_2SO_4 (abs. of traces of nitrates and nitrites). With pure aluminium or zinc it must evolve pure hydrogen gas, which does not stain paper moistened with silver nitrate. After conversion into chloride it must give a pure potassium spectrum.

PREPARATION. Potassium hydrate is made by decomposition either of carbonate by calcium hydrate, or of sulphate by barium hydrate, or of nitrate by metallic copper. According to the purity of the ingredients a more or less pure product is obtained. Carbonate derived directly from wood-potash or from various potassium minerals is apt to contain many impurities, while that obtained from bicarbonate or from purified cream of tartar furnishes better results. The more impure varieties of commercial hydrate may be purified by solution in strong alcohol (free from aldehyde, fusel oil, etc.), which leaves most impurities undissolved, evaporating and fusing the dry residue. That resulting from careful decomposition of pure sulphate by barium hydrate is pure. So is that occasionally made from pure metallic potassium. In all

operations requiring heating (or even preservation) of potassium hydrate in concentrated solution or fusion, vessels of glass, porcelain or platinum must be avoided and iron or, still better, silver used. Access of air must be avoided as much as possible, as its CO_2 is absorbed with great avidity.

To prepare the hydrate from carbonate 2 parts of potassium carbonate are dissolved in 24 parts of water, the solution heated to boiling and 1 part of pure, freshly-slacked lime added gradually in small portions, with frequent stirring and occasional replacing of the evaporated water. When a small portion of the filtered liquid no longer effervesces with acid, the mixture is covered and set aside to deposit the calcium carbonate; the clear liquid is then removed by decanting or by a syphon, carefully protected from the CO_2 of the air and may be used directly as a test solution, or for preparing normal solution, or evaporated in a silver dish and fused. From potassium sulphate the hydrate is prepared by carefully neutralizing a solution of 16 parts of crystals of barium hydrate in 48 parts of boiling water, by adding pure potassium sulphate (about 9 parts) until a small filtered portion no longer gives a precipitate with potassium sulphate. The mixture is covered and set aside until the barium sulphate has subsided; it is then decanted, evaporated to dryness and, if necessary, freed from a trace of sulphate by re-solution in strong alcohol and evaporation. *Wœhler* directs heating to redness in a copper crucible 3 parts of fine cut metallic copper with 1 part of pure saltpetre and leaching out with water.

Normal potassium hydrate is made either by using the solution obtained in the above processes, or dissolving a fair commercial hydrate, *free from carbonate*, and standardizing by means of normal acid. The solution then contains 55.979 gr. of KOH in one litre.

POTASSIUM HYPOCHLORITE, $KClO$, is sometimes used instead of the sodium salt as a source of chlorine; for oxidation of nickelous to nickelic salt; for solution of arsenic spots in Marsh's test, and, instead of hypobromite, for liberation of N from urea. It is made by precipitating a solution of calcium hypochlorite by potassium carbonate.

POTASSIUM IODATE, KIO_3.

USES. To furnish, by adding sulphuric acid, iodic acid to detect reducing alkaloids by liberation of iodine, e. g., to distinguish morphine, which rapidly reduces, from codeine. $KIO_3 = 213.456$.

TESTS. Potassium iodate crystallizes in the regular system; at 15° C. it dissolves in 13 parts of water; at 560° it melts and sepa-

rates into potassium iodide and oxygen. The residue may then be tested for purity as directed for potassium iodide. The commercial salt is pure enough for use.

PREPARATION. 12.7 parts of iodine are diffused in water and chlorine passed into it until the iodine has completely dissolved; 12.2 parts of potassium chlorate are then added and heat applied until no more chlorine escapes. On cooling, crystals of iodate form, which are purified by recrystallization.

POTASSIUM IODIDE, K I.

USES. For detection of lead, silver, mercury, palladium, etc., by colored precipitates. For preparation of volumetric and other test solutions of iodine, of mercuric iodide, Nessler's, Mayer's, etc. For the absorption of chlorine, which liberates iodine and may thus be determined by solution of sodium hyposulphite. With starch paste as indicator of ozone, nitrous acid, chlorine, bromine, etc. Mixed with sulphur as a blowpipe reagent for bismuth. Also in 25% solution in water to extract the coloring matter of old bloodstains for examination by the spectroscope (*Helwig*). K I = 165.576.

TESTS. Pure potassium iodide crystallizes in colorless transparent cubes (the white porcelain-like crystals are generally due to crystallizing from alkaline solution, octohedra are formed when free iodine is present). At 15° C. it dissolves in 0.714 parts, at 100° C. in 0.48 parts of water; it is also soluble at 15° in 20 parts absolute alcohol. At 634° it melts, and at higher temperature is vaporized; at 200° it absorbs oxygen and becomes contaminated with iodate (*Petterson*). For many purposes small amounts of chloride, sulphate or sodium do not interfere with its use, but iodate and carbonate must be absent in all cases. The pure salt must not give alkaline reaction when laid on moist testpapers. On addition of dilute sulphuric acid it must not effervesce nor color a starch solution blue. Neither must free iodine be liberated by nascent hydrogen (zinc and H Cl). The absence of cyanogen is shown by heating the solution with a little ferrous sulphate, ferric chloride and potassium hydrate; after acidulation no blue color must appear. The absence of chloride is shown by digesting the well-washed precipitate formed with silver nitrate in ammonia and then acidulating with nitric acid, only a slight opalescence must be produced. Barium chloride must give no precipitate. Flame color and spectrum must be pure. The absence of metallic impurities is shown, as in other potassium salts.

PREPARATION. Potassium iodide free from iodate is best obtained on the laboratory scale by Frederking's modification of Baup's process. 17 gr. of pure, fine, iron wire, in short pieces, are covered with 100 Cc. water, and 75.8 gr. of pure iodine, in fine powder, gradually added. After solution of nearly all the iron and filtering, 25.2 gr. of iodine are dissolved in the solution, so as to form $Fe_2 I_6 . Fe I_2$, and then pure potassium carbonate added as long as a precipitate of ferric hydrate falls (requiring 55 gr. of dry $K_2 C O_3$), the mixture is filtered, heated and, if more precipitate falls, filtered again, evaporated and crystallized.

A stable solution of starch and potassium iodide is obtained by placing in a capacious flask 5 gr. of fine starch and 50 Cc. water. After thorough shaking, the adhering starch particles are washed down by a spritz-flask, and 25 Cc. of solution of 1 part of pure potassium hydrate in 2 parts of water added. Strong shaking will now produce a uniform gelatinous mass. To this 2 gr. potassium iodide dissolved in 500 Cc. of water are added, and the mixture heated to boiling with constant agitation. After cooling, the clear solution is diluted to one litre, and will now remain undecomposed for a great length of time (*Reinhardt*).

POTASSIUM NITRATE, $K N O_3$.

USES. Besides its use for the preparation of potassium hydrate, nitrite and nitric acid, potassium nitrate serves as an oxidizer of carbon, of sulphides, and, especially in blowpipe work, for recognition of chromium salts by conversion into yellow potassium chromate; in assaying for making black, gray and white flux and uncombined for oxidation of the sulphides of silver, copper and lead. Also for making solution for standardizing indigo solution. In many cases sodium nitrate is now used instead of the potassium salt. $K N O_3 = 100.920$.

TESTS. Potassium nitrate forms colorless, rhombic prisms, soluble at 15° C. in 4 parts, at 100° in 0.5 parts of water, nearly insoluble in alcohol. The tests for metallic impurities are the same as for other potassium salts. The solution must not be rendered turbid by silver or barium nitrate, must show no precipitate with ammonium molybdate, nor give arsenic reactions by Gutzeit's test (see, on page 117, ferrous sulphide). It must be neutral to test-papers. With chlorine water and starch solution no iodine or bromine reaction should be given.

PREPARATION. On a small scale, pure potassium carbonate may be neutralized with pure nitric acid and crystallized. Commercial saltpetre is purified by repeated recrystallization, rejecting the first crystals, which contain the less soluble earthy salts, as

well as the mother-lye containing the more soluble chlorides. The crystals are, by stirring, obtained as small as possible, to prevent enclosure of mother-lye. The crystalline powder is then placed upon a funnel to drain, covered with filter-paper and moistened, first, with a saturated solution of pure nitrate, which, on percolating, withdraws soluble impurities, then with a little pure water, and, finally, dried.

POTASSIUM NITRITE, $K\,N\,O_2$.

USES. To detect cobalt and separate it from nickel, etc., as *Fischer's* salt (presence of calcium, strontium, barium and lead interferes); for conversion of aromatic amines into di-azo compounds and various color reactions based upon this process (*Weselsky, Ehrlich*). With sulphuric acid for the recognition of various phenols by characteristic colors (*Liebermann*), and of antipyrine by the green color of the nitroso compound. A standard solution is used in conjunction with starch and zinc iodide for comparison with specimens of drinking water tested for nitrites by the colorimetric method, the depth of color of starch blued by the iodine liberated by nitrites serving as a means of determining the quantity. A solution of a small quantity of potassium nitrite (or of $N_2\,O_3$) in nitric acid is sometimes used as *Plugge's reagent* to distinguish antifebrin (acetanilide), which is colored red, from phenacetin, which remains unaffected. The reaction is analogous to that produced by mercurous nitrate with free nitrous acid (also called Plugge's reagent) on phenol. $K\,N\,O_2 = 84.96$.

TESTS. Potassium nitrite is usually sold in fused masses or pencils, very deliquescent and often impure. For most purposes the presence of a small amount of nitrate is not objectionable, but metallic impurities, chloride and sulphate must be absent, and may be detected as in other potassium salts.

PREPARATION. Potassium nitrate is fused with twice its weight of lead, the mass being constantly stirred until the lead is oxidized. It is then leached out with cold water, filtered and carbonic acid passed into the solution to precipitate the lead. After filtering, nitric acid is added to neutralize any carbonate and the liquid evaporated. The first crystals, containing nitrate of potassium and lead, are rejected and from the residue small prismatic crystals of potassium nitrite are obtained. If $H_2\,S$ should still show a trace of lead in these, and it is necessary to remove this, the crystals are fused for about 12 hours, to decompose the rest of the lead salt and render it insoluble. The residue is recrystallized and carefully preserved. The *standard colorimetric* solution is made by decomposing 0.406 gr. of pure silver nitrite by a slight excess of pure

potassium chloride, diluting with water to 1 litre and filtering. Each 1 Cc. corresponds to 0.01 milligr. of N_2O_3. See also *silver nitrite*, *starch* and *zinc iodide*.

POTASSIUM NITROPRUSSIDE, $K_2Fe . NO . (CN)_5 + 2 H_2O$, is proposed as a reagent for albumin in urine (*Mya*). In action it is similar to the ferrocyanide and does not differ from that of the sodium salt, see *sodium nitroprusside*.

POTASSIUM OXALATE.

USES. The several oxalates have been used, instead of oxalic acid, as reducents, etc., and especially for standardizing volumetric solution of potassium permanganate, but only the

TETROXALATE, $KHC_2O_4 . H_2C_2O_4 + 2 H_2O$, deserves notice. On account of its permanence in composition and great stability in solution it is recommended as starting point for alkalimetric and oxidimetric solutions (*Kraut*, *Albricht*, *Meissl*). Mol. W. = 253.515.

TESTS. Potassium tetroxalate (quadroxalate) crystallizes in transparent, monoclinic prisms, which dissolve at 13° C. in 55.25 parts of water, more readily in boiling water, and become anhydrous at 126° C. The salt is tested as directed for other potassium salts for absence of metallic impurities, and of nitrate, chloride and sulphate.

PREPARATION. Either by mixing boiling hot solutions of 1 part of potassium carbonate and 2.1 parts of oxalic acid, crystallizing and recrystallizing in very small crystals from boiling water; or by purification of the commercial salt. This consists principally of a mixture of $KHC_2O_4 + H_2O$ with $KHC_2O_4 . H_2C_2O_4 + 2H_2O$. The amount of oxalic acid necessary to convert it into tetroxalate is ascertained by titration with normal potassium hydrate, and a slight excess of this amount is mixed with the salt in boiling solution. On cooling the crystallization is interrupted so as to obtain small crystals. These are placed on a funnel to drain and are washed with a little very cold water to remove more soluble impurities until the filtrate no longer shows impurities. If necessary, another recrystallization from boiling water is resorted to. The salt is dried at a low temperature in an exsiccator.

Potassium ferrous oxalate, see page 117.

POTASSIUM PERMANGANATE, $KMnO_4$.

USES. The readiness of potassium permanganate to yield its oxygen makes it a valuable agent in a variety of operations in volumetric analysis. With the addition of sulphuric acid it serves to convert oxalic acid into carbon dioxide : $2 KMnO_4 + 5 H_2C_2O_4 +$

$3 H_2 S O_4 = K_2 S O_4 + 2 Mn S O_4 + 10 C O_2 + 8 H_2 O$. The intense purple-red solution of permanganate being during the reaction converted into the almost colorless manganous sulphate, so that the end of the process is sharply indicated by a single drop of permanganate in excess, giving a permanent rose-red color. Organic substances in drinking water are in similar manner determined, and conventionally estimated by assuming them to be five times the amount of the potassium permanganate used in their oxidation (*Kubel*, *Woods*, *Mohr*, *etc.*) Ferrous salts are in like manner converted into ferric and by various modifications of this process, direct or indirect, quite a variety of substances are volumetrically determined. It is also used for titration of spir. ætheris nitrosi, etc. Methyl alcohol reduces dilute solutions of permanganate very rapidly, ethyl alcohol rather slowly, so that it may serve to differentiate the alcohols (*Cazeneuve and Cotton*). Also to aid in the conversion of the nitrogen of organic matters into ammonium salts, in *Kjeldahl's* and *Wanklyn's* processes. Also as *Wenzel's* reagent (1 $K Mn O_4$ in 200 $H_2 S O_4$) for alkaloids. Also with indigo as indi cator for titration of tannin (*Loewenthal*, *Neubauer*). Mixed with dilute sulphuric acid it serves to detect hydrastine by the production of intense blue fluorescence, which disappears by further oxidation (*Lyons*). Also for the purification of carbon disulphide. $K Mn O_4 = 156.765$.

TESTS. Potassium permanganate crystallizes in long rhombic prisms of dark metallic lustre, deep purple-red by transmitted light. Soluble in 16 parts of water at 15°, in 2 parts at 100° C. When absolutely pure, 213.53 parts of potassium permanganate should require 448.94 parts of oxalic acid for complete decomposition. But for nearly all purposes a good commercial article is sufficiently pure as the volumetric solution is not made by solution of a definite weight, but by adjusting the titre by a standard solution. When it is to be tested for nitrates and chlorides the solution is first decomposed by oxalic acid and the tests applied to the colorless liquid. To test for sulphate the solution is boiled with excess of ammonia until all the manganese is precipitated, and then the barium salt added to the acidulated filtrate.

PREPARATION. Of the various processes for preparing the salt on a laboratory scale, free from other salts, that of *Squibb* is very suitable. A mixture of the purest manganese dioxide and potassium hydrate is heated almost to redness, and then a little water sprinkled upon it and the process of heating and sprinkling repeated several times. The mass is finally leached out with boiling water, the crystals repeatedly purified by recrystallization, and the product dried and preserved in the dark.

Volumetric solutions of various strengths are made either empirical, so that 1 litre corresponds to 10 gr. of metallic iron, or as directed by the U. S. P., 1 gr. to be dissolved in 1,000 Cc. of water; or in the system, generally deci-normal, and for water analysis centi-normal. As 2 mol. of $K Mn O_4$ furnish the necessary oxygen for converting 5 mol. of $H_2 C_2 O_4$ into $C O_2$, and as oxygen is diatomic, one-fifth of the molecular weight or 31.353 gr. are necessary for 1 litre of normal solution and a corresponding quantity for deci and centi-normal. As ordinarily made these solutions change titre rapidly, hence the necessity of taking the titre frequently, so as to make corrections for the changes. A *very stable* solution may be made by mixing in proper proportions two solutions, one stronger and one weaker than required, both having been boiled and left in a dark place for several days to deposit precipitate. The titre is adjusted either by oxalic acid, potassium tetroxalate, metallic iron, ammonium ferrous sulphate, potassium ferrocyanide, ammonium sulphocyanate or vanadium pentoxide, and the solution kept in clean, glass-stoppered bottles, protected from light.

POTASSIUM ACID PYRO-ANTIMONATE, $K_2 H_2 Sb_2 O_7 + 6 H_2 O$.

USES. This salt, which is often, though improperly, called the *acid met-antimonate* or simply *antimonate*, serves to detect sodium salts by precipitating from their neutral or alkaline solution the very sparingly soluble $Na_2 H_2 Sb_2 O_7 + 6 H_2 O$, which to the naked eye appears amorphous, but under the microscope shows boat-shaped, quadratic octahedra and prisms, which deposit themselves first on the parts rubbed with a stirring rod. In aqueous solution the reagent decomposes slowly at ordinary temperature, more rapidly by boiling, forming (gummy) ortho-antimonate: $K_2 H_2 Sb_2 O_7 + H_2 O = 2 K H_2 Sb O_4$, which is much more soluble in water. This salt also precipitates sodium as $2 Na H_2 Sb O_4 + 3 H_2 O$, but is not as delicate a reagent as the unchanged pyro-salt, for the sodium ortho-antimonate is at first quite soluble and changes into an insoluble variety only after long standing. Mol. W. = 530.428.

TESTS. The salt is usually obtained in granules, requiring for solution 250 parts of water at 15° C., 90 parts at 100°. As it is only used in qualitative work, the only test prescribed by *Fresenius* is that the solution must not give precipitates with potassium or ammonium chloride, but a copious one with sodium chloride.

PREPARATION. Antimonic acid is fused with a large excess of potassium hydrate, the mass dissolved in water and evaporated until granular masses of neutral pyro-antimonate, $K_4 Sb_2 O_7$, separate. These are removed from the motherlye, drained and left in contact with about 20 parts of water for several hours. The salt

separates into acid pyro-antimonate and caustic alkali; the granules are drained, washed with a little water and preserved until needed. *Brunner* directs deflagrating in small portions a mixture of equal parts of tartar emetic and saltpetre fluxing the residue until it flows quietly and, after cooling, extracting the mass by boiling water. On cooling, the salt separates as a heavy, white powder.

The solution should only be made shortly before it is needed, and then only with cold water.

POTASSIUM STANNOUS CHLORIDE, $Sn\,Cl_2 . 2\,K\,Cl + H_2O$.

USES. This double salt produces in nearly neutral solutions of sodium, ammonium and lithium white precipitates, and thus serves for their detection, especially that of sodium, in solutions in which only alkali salts must be present; alcohol, free acids and borates also interfere with the reaction; carbonates must be neutralized by hydrochloric acid (Hager). Mol. W. = 355.226.

PREPARATION. Five grammes of stannous chloride in crystals dissolved in 10 Cc. of water and 6.5 gr. of potassium hydrate, dissolved in 40 Cc. of water, are mixed, reserving a little of the potassium solution. After the mixture has stood for an hour and deposited any insoluble matter, it is decanted and the rest of the potassium solution, diluted with 15 Cc., is added. After several hours standing in a close vessel the solution is filtered and carefully preserved. Long exposure to air might oxidize and produce stannic salt, by whose presence rubidium would be precipitated.

POTASSIUM STANNOUS SULPHATE, $K_2S\,O_4 . Sn\,S\,O_4$.

USES. For the titration of nitric acid. The reaction depends upon the conversion of the stannous into the stannic sulphate at the expense of the oxygen of the nitric acid, presence of a considerable excess of sulphuric acid being necessary. $4\,(K_2S\,O_4 . Sn\,S\,O_4) + 4\,H_2S\,O_4 + 2\,H\,N\,O_3 = 4\,K_2S\,O_4 + 4\,Sn\,(S\,O_4)_2 + N_2O + 5\,H_2O$. The solution is colored blue by diphenyl-amine and remains so until the nitric acid is completely reduced, when it becomes colorless (*Longi*). $K_2S\,O_4 . Sn\,S\,O_4 = 387.384$.

PREPARATION. Stannous sulphate is first made by adding an excess of pure tin to hot, concentrated, pure sulphuric acid. A white salt results, which dissolves in 5.5 parts of water, hot or cold. Of this salt 11 parts are mixed with 9 parts of pure neutral potassium sulphate and dissolved in 65 parts of boiling water. The solution on cooling and after evaporation deposits silky crystals of the double salt, which are purified by recrystallizing.

Decinormal solution containing 37.7884 gr. of the dry anhydrous salt, corresponding to 11.7698 gr. of metallic tin, is made by dissolving 40 gr. in 800 Cc. of 50% sulphuric acid, spec. gr. 153. If any residue remains undissolved a minimum of conc. hydrochloric acid is added to dissolve it, and then the strength of the solution is ascertained by a deci-normal solution of potassium nitrate (10.092 gr. $K N O_3$ in 1 litre) after addition of a large excess of sulphuric acid and a drop of solution of diphenyl-amine. From the ascertained strength of the stannous solution the titre is carefully adjusted by dilution with dilute sulphuric acid to deci-normal strength, so that it runs accurately together with the deci-normal nitrate. Whenever a specimen of nitric acid or nitrate is to be tested it is after weighing, diluted and at least 3.5 volumes of sulphuric acid and a drop of diphenyl-amine added before titration with the stannous solution.

POTASSIUM SULPHATE.

a. NEUTRAL POTASSIUM SULPHATE, $K_2 S O_4$.

USES. To precipitate barium, strontium and lead salts by converting them into insoluble sulphates, without introducing free acid into the solutions. Also for preparing pure potassium hydrate, potassium stannous sulphate, etc. To detect aluminium salts by the octahedral crystals of alum formed by mixing concentrated solutions, especially used as microchemical test. $K_2 S O_4 = 173.882$.

TESTS. Pure potassium sulphate forms colorless, rhombic prisms, terminating in pyramids, much resembling the hexagonal crystals of quartz. It is soluble in about 9.1 parts of cold and 4 parts of boiling water, insoluble in absolute alcohol. It is tested for metallic impurities like other potassium salts and should give no acid reaction with test papers, no precipitate with silver nitrate or ammonium molybdate, no blue color with diphenyl-amine and sulphuric acid, nor leave an insoluble residue after evaporation to dryness with hydrochloric acid.

PREPARATION. The commercial salt usually obtained as a bye-product of various operations, is liable to be contaminated with different impurities derived from such origin, but may be obtained pure enough for most purposes by careful, repeated recrystallization. On a small scale, it may be obtained by saturating pure bicarbonate with pure sulphuric acid. The test solution contains 1 part in 12 parts of water.

b. ACID POTASSIUM SULPHATE, $K H S O_4$.

Potassium bi or di-sulphate.

USES. In conjunction with potassium permanganate for liberation and removal of bromine and its separation from chlorine (*Berglund*). Also as a flux for decomposing and rendering soluble ores and minerals insoluble in acids, emery, corundum and other aluminium compounds, rutile, sphene and other titanium minerals, chromic iron ore, etc., and for cleansing platinum crucibles. $K H S O_4 = 135.863$.

TESTS. Potassium acid sulphate crystallizes from acid solutions in rhombic tables. It melts at 200° C., and, on cooling, forms monoclinic crystals. At 15° C. it dissolves in 2.3 parts of water, at 100° in 0.9. From the aqueous solution neutral sulphate crystallizes first. It is tested like the neutral sulphate, but contains double the amount of acid, as may be tested by titration with potassium hydrate and phenol-phthalein.

PREPARATION. The salt is obtained as a bye-product in the manufacture of nitric acid from saltpetre, etc. It is made pure on the small scale by melting together in a platinum vessel 13 parts of pure neutral sulphate with 8 parts of pure conc. sulphuric acid and discontinuing the heat as soon as white vapors of sulphuric acid begin to escape, or by adding to the above ingredients 42 parts of water, evaporating almost to dryness and collecting the crystals, which are then recrystallized from a minimum of water, acidulated strongly with sulphuric acid to prevent the separation of neutral salt.

POTASSIUM SULPHIDE, in the crude commercial state (hepar sulphuris), is used to render hydrogen sulphide free from arsenic, by passing the dry gas through long tubes filled with lumps of fused hepar and heated to 350° C. (*Von der Pfordten*).

POTASSIUM SULPHOCARBONATE, $K_2 C S_3$, is used for detection of cobalt and nickel. Even in very dilute solution, made alkaline by ammonia, this reagent colors nickel orange; cobalt, wine-yellow (*Braum*). Also as a substitute for $H_2 S$, to precipitate solutions of metals (*Hager*). It is prepared according to *Fresenius* by dividing a 5% solution of potassium hydrate in two equal parts, saturating one-half with $H_2 S$, digesting the other half with about 1-25th of its volume of carbon disulphide, and after removal of the surplus of $C S_2$ mixing the solutions. A dark orange-colored solution results, which must be carefully preserved, as it decomposes rapidly in contact with air into free sulphur and potassium carbonate.

POTASSIUM SULPHOCYANATE, K C N S.

Sulphocyanide, Thiocyanate or Rhodanate.

USES. For the detection of ferric salts, which produce with it a deep red color, even in great dilution; this is interfered with by the presence of alkaline citrates, malates, tartrates, etc. Also for detection of nitric and nitrous acid, which with concentrated solutions produce a blood-red color similar to iron, which gradually fades on heating or dilution. Also to detect cupric salts, which, after reduction by $S\,O_2$, give a white precipitate of cuprous sulphocyanate. Also instead of ammonium sulphocyanate in deci-normal solution for titration of silver, according to *Volhard*. See page 40. K C N S = 96.998.

TESTS. Pure potassium sulphocyanate crystallizes in colorless, transparent, rhombic prisms, similar to saltpetre. It is very deliquescent, dissolving in 0.5 parts of water at 15° C., and producing great cold while dissolving. Soluble in 10 parts of absolute alcohol. The aqueous solution must not be precipitated by barium chloride; pure hydrochloric acid must not produce a red color; ammonium sulphide must produce color or precipitate.

PREPARATION. A mixture of 17 parts of dry potassium carbonate, 46 parts of anhydrous potassium ferrocyanide and 32 parts of sulphur is, by gradual increase of heat, fused and finally heated to redness to destroy any hyposulphite formed. After cooling, the mass is leached out by boiling alcohol and purified by repeated crystallization from alcohol, so as to remove all impurities insoluble in it. The test solution contains 1 part in 10 of water. Deci-normal solution contains 9.6998 gr. in 1 litre, but can not be made by direct weighing on account of the great deliquesence of the salt, but must be made stronger and then standardized by deci-normal silver nitrate, just as the ammonium salt, page 40.

POTASSIUM ANTIMONOUS TARTRATE, $2\,[K\,(Sb\,O)\,C_4\,H_4\,O_6] + H_2\,O$, *tartar emetic*, has been used in volumetric solution for titration of tannic acid (*Gerland*), but the method is not a very accurate one. Mol. W. = 663.14. The commercial salt is sufficiently pure when recrystallized.

Potassium tetroxalate, see *oxalate*, page 168.

QUARZ, $Si\,O_2$.

Natural crystals of silicic acid in small fragments, sometimes used as material for filtering acids, or coated with platinum or other metals for operations at high temperature, etc. See the article *Asbestus*, page 46.

RESORCIN, $C_6H_4(OH)_2$.

USES. Resorcin, or *meta-di-oxy-benzol*, is a very delicate reagent for iodoform, chloroform and chloral hydrate. When a small quantity of resorcin is dissolved in a slight excess of potassium hydrate solution it produces an intense red color, due to the formation of rosolic acid, on heating it with even traces of iodoform (*Lustgarten*), of chloroform or chloral hydrate (*Schwarz*). The reaction is especially adapted to finding traces of these substances in urine. Small amounts of ferric chloride may be identified by this reagent by producing a violet blue color. It also serves for the detection of saccharin, Fahlberg (ortho-sulphamine benzoic anhydride, or benzoic acid sulphinide, $C_6H_4 . CO . SO . NH$), which is now extensively used as a substitute for sugar; on addition of resorcin and a few drops of concentrated sulphuric acid to a small amount of saccharin and heating, the liquid assumes, in succession, a yellow, red and then a dark green color, while SO_2 escapes with effervescence. If, after cessation of this effervescence, the liquid is made slightly alkaline by potassium hydrate, a strong, green fluorescence indicates the presence of saccharin (*Ira Remsen*). It is also used for the detection of carbohydrates (*Ihl*, modified by *Molisch*), especially glucose, which gives a red color when brought together with an alcoholic solution of resorcin and floated on conc. sulphuric acid. By melting resorcin with sodium hydrate phloroglucin is obtained. Mol. W. = 109.764.

TESTS. Resorcin forms small, colorless, rhombic prisms, melting at 110° C.; subliming at 276.5°. It dissolves in 0.67 parts of water at 12.5° C., and easily in alcohol and ether. Its aqueous solution should not form a precipitate with lead acetate (abs. of pyrocatechin). It should sublime without residue. The commercial article is sufficiently pure if not browned by exposure to air and light. If such is the case, it must be carefully resublimed.

PREPARATION. A somewhat impure product, difficult to purify completely, is obtained by melting ammoniacum, galbanum, asafœtida or xanthorrhœa resin with caustic alkali and extracting the fused mass by ether. A better product is obtained on the small scale by fusing potassium or calcium benzol-meta-disulphonate with potassium hydrate, dissolving the fluxed mass in acidulated water, extracting the resorcin with ether and subliming the residue remaining after distilling off the ether at 276.5° C. On the large scale resorcin is made by adding gradually, in a thin stream and with a constant stirring, 24 parts of benzol to 90 parts of fuming sulphuric acid, contained in a cast iron still, provided with stirring apparatus and leaden condenser. After keeping up the

stirring for two or three hours, the benzol disappears, the heat is then raised to 275° C., when a little benzol and water distill over. The temperature is kept up for some time and the mixture, now containing *benzol-meta-disulphonic acid*, is then poured into 2,000 parts of water and neutralized by milk of lime. Calcium sulphate precipitates and is separated, and the solution contains calcium benzol-meta-disulphonate. The filtrate is evaporated to dryness and 60 parts of the dry salt are mixed with 150 parts of caustic soda and very little water, and kept for eight or nine hours at a temperature of 270° C. The acid is thereby converted into resorcin. The mass is dissolved in 500 parts of boiling water, a little hydrochloric acid added and boiled to expel $S\,O_2$. After cooling, the liquid is shaken with ether in a suitable apparatus, the ethereal solution is separated, the ether distilled off and the residue of resorcin sublimed at 276.5° C.

RUTHENIUM CHLORIDE is used to detect hyposulphites (thiosulphates), even in traces, by assuming with them in presence of ammonia an intense red color, visible yet in great dilution (*Carey Lea*). $Ru_2\,Cl_6 = 415.22$.

SAFRANINE HYDROCHLORATE, $C_{21}\,H_{20}\,N_4 \,.\, H\,Cl$.

USES. Commercial safranine (the hydrochlorate) has been introduced by *L. Crismer* as a most delicate reagent for the detection of glucose, especially in urine, and of disaccharides and glucosides, after heating them with dilute acid. It is a di-azo-derivative of ortho-toluidine, and yields with water or alcohol red solutions (often used for staining tissues in microscopical work or for coloring wine); the solution in presence of alkali is rendered pale yellow by reducents, zinc dust, nascent hydrogen, glucose, ferrous salts, etc., forming a leuco-compound similar to that of indigo. This reduction occurs very slowly at ordinary temperature, but rapidly above 60° C. A solution of 1 gramme of safranine in a little alcohol and diluted to 1 litre with water is used for detection of glucose in urine. Of this 5 Cc. are used for 1 Cc. of urine, 2 Cc. of solution of sodium hydrate added and heat applied. The small trace of reducent present in normal urine (generally supposed to be glucose) does not suffice to reduce this amount of safranine, so that, if the color becomes yellow, an *abnormal amount of glucose* must be present. Shaking with air, or standing in contact with it, restores the color, so that for delicate testing of small amounts a layer of paraffin oil may be used to prevent access of air.

Albumin decolorizes the safranine solution slowly but completely; urates, creatinine and other normal constituents of urine do not affect it, neither does chloral hydrate or chloroform.

TESTS. The commercial article is sufficiently pure. It might be tested with a small amount of glucose to ascertain its efficiency. The brown-red crystals have, when dry, a greenish, metallic lustre, and are very soluble in water or alcohol. A small crystal thrown into concentrated sulphuric acid dissolves with a deep green color, which, by gradual addition of water, drop by drop, turns, first, a deep indigo blue, then violet and, finally, red.

PREPARATION. Ortho-toluidine is treated with nitrous acid, which affects di-azotation by uniting the nitrogen of two of the three amido-groups present in three toluidine molecules, so that $.NH_2 + .NH_2 = .N:N. + 2H_2$. The product is then oxidized by means of potassium dichromate. The crystals are then purified by recrystallization from very dilute, hot hydrochloric acid.

Nigrosine and *induline* may be substituted for safranine and are similarly decolorized.

Scheibler's Reagent, see *phospho-tungstic acid*, page 18.

SILVER AND ITS COMPOUNDS.

SILVER, Ag.

USES. Pure metallic silver is used for preparing various salts; for adjusting the titre of volumetric solution of sodium chloride; in docimastic assay for alloying with gold, in the *quartation* process. In the state of fine powder or fine wire netting for absorption of chlorine, bromine and iodine. Also in elementary organic analysis in fine turning chips instead of copper turnings, to decompose the oxides of nitrogen formed during combustion. Ag = 107.675.

TESTS. Pure silver has spec. gr. 10.57; it melts at about 1,000° C. and at bright white heat may be distilled; while melted it absorbs oxygen, most of which again escapes on solidifying. It is insoluble in hydrochloric acid, soluble in nitric and in conc. sulphuric. Its solution in nitric acid must, after precipitation with dilute hydrochloric acid, yield a filtrate which, on evaporation, leaves no residue.

PREPARATION. Coin silver or silver bullion is dissolved in nitric acid, the solution decanted and precipitated by dilute solution of pure sodium chloride, and the precipitated silver chloride is, after thorough washing, reduced to the metallic state, either by drying, fusing and digesting with pure zinc and dilute hydrochloric acid, or by fusing with dry sodium carbonate and borax, or by boiling with sodium hydrate and glucose solution. For use as an absorbent of chlorine, etc., in the analysis of organic compounds, silver,

in fine powder, is sometimes sprinkled over asbestus, or the asbestus is soaked in solution of silver nitrate, dried and exposed to the vapor of H Cl, and finally heated in a current of hydrogen to reduce the chloride coating to metal.

For preparing ABSOLUTELY PURE SILVER for determination of atomic weights *Stas* gives the following directions: Silver nitrate is fused to decompose any platinic nitrate present, dissolved in dilute ammonia water, and, after standing for 48 hours, is filtered and diluted so as to contain about two per cent of silver. A slight excess of ammonium sulphite is added, if Cu was present, until the disappearance of the blue color. The solution is then heated to between 60° and 70° C., when all the silver is reduced to metal and precipitates in form of fine powder. This, after cooling, is washed by decantation with successive portions of ammonia water until the washings show absence of copper and sulphuric acid. The powder is set aside to digest for several days with a fresh portion of ammonia, then washed with water and dried. It is either preserved as powder or fused with dry sodium carbonate and borax.

SILVER NITRATE, $Ag\,N\,O_3$.

USES. As a group reagent for the detection and precipitation of inorganic acids of the second group (H Cl, H Br, H I, H C N, etc.) and for their separation from the acids of the third group ($H\,N\,O_3$, etc.), which form soluble silver salts; as well as for the titration of the precipitable acids by volumetric solutions. It also serves as a special reagent for distinguishing, by colored precipitates, chromic acid (red), arsenous acid (yellow, Hume's test), arsenic acid (red-brown), etc. Also by suffering reduction to metallic silver, especially in alkaline solution, formic acid, chloroform, chloral hydrate, tartaric acid, glucose, aldehydes (*Tollens*), etc. Also for detection of arsenetted hydrogen in Fleitmann's, Gutzeit's and other tests; the test tube in which the gas is evolved is covered with a cap of filter paper upon which a drop of solution of silver nitrate is placed. If this solution is dilute the arsenetted hydrogen at once reduces the silver to the metallic state and thereby produces a dark spot, but, if a saturated solution is used, a yellow compound, $Ag_3\,As\,(Ag\,N\,O_3)_3$, is formed, which is decomposed by water and separates black metal. $Ag\,NO_3 = 169.576$.

TESTS. Silver nitrate forms colorless, rhombic plates, soluble at 15° C. in 0.5 parts of water and in 26 parts of alcohol of 95%. At 218° it melts without decomposition and crystallizes on cooling. In the commercial salt silver chloride or potassium nitrate are sometimes found, also copper, etc. To detect the two former, 1 part of the nitrate is dissolved in 1 part of water and 40 parts of

absolute alcohol added; if pure, no precipitate must fall. If the aqueous solution is fully precipitated by dilute hydrochloric acid, the filtrate must, on evaporation, leave no residue, even if a larger quantity of silver nitrate is thus tested. The washed precipitate may be dried and weighed and 1.69576 gr. of silver nitrate should yield 1.43045 gr. of chloride.

PREPARATION. Pure silver is dissolved in a slight excess of pure nitric acid, evaporated to dryness and fused. Of this, for ordinary test solution, 1 part is dissolved in 20 parts of water. For deci-normal solution 16.9576 gr. are dissolved in 1 litre. If a salt of less purity must be used, a stronger solution is made and diluted to the standard of pure, deci-normal sodium chloride.

Toilens' reagent for glucose and aldehydes is made by dissolving 1 gr. of silver nitrate in 10 gr. of ammonia water of spec. gr. 0.923 (21% NH_3) and adding 1 gr. sodium hydrate dissolved in 10 Cc. of water. It must be carefully preserved in the dark, and as after drying it forms a dangerous explosive, it is safest to make it only as needed. On addition of this reagent to solutions of glucose or aldehyde metallic silver is reduced, generally as a mirror coating the test tube.

SILVER NITRITE, $AgNO_2$.

USES. To adjust the titre of empirical potassium permanganate solution, when it is to be used for titration of nitrites, or for the preparation of a standard solution of potassium nitrite for colorimetric determination of nitrites in water. $AgNO_2$ =153.616.

TESTS. Silver nitrite forms pale yellowish prisms, sparingly soluble in cold, more easily in hot water. At 90° C. it begins to decompose, forming nitrate, metallic silver and nitrogen dioxide. Light produces a similar effect. It is tested for impurities like the nitrate.

PREPARATION. Solutions of 17 parts of silver nitrate and 10 parts of potassium nitrite, each in a minimum of water, are mixed. The precipitate is washed, dried and preserved with exclusion of light.

SILVER OXIDE, Ag_2O, is sometimes used to remove chlorine without introducing another acid radical or disturbing neutrality. It is made by precipitating silver nitrate by potassium hydrate.

SILVER SULPHATE, Ag_2SO_4, is used for similar purposes as the oxide, especially for removing barium chloride from solution of hydrogen dioxide. It is made by dissolving silver in boiling conc. sulphuric acid, or precipitated by conc. sulphuric acid from saturated solution of silver nitrate.

SKIN POWDER is used for removal of tannin from vegetable extracts and determining its quantity by difference in specific gravity (*Hammer*).

SOAP SOLUTION.

USES. To ascertain the degree of hardness of water, i. e., its contents of lime and magnesia salts. The method, as derived by *Clark* and improved by *Faisst* and *Knauss*, depends upon the fact that pure water shaken with pure soap produces a copious foam, while in hard water the soap is converted into insoluble lime and magnesia compounds, and foaming will not occur until after the complete precipitation of these salts. The end of the reaction is the production of foam standing for 5 minutes. The result is expressed in *degrees of hardness*, which differ in different countries. In Germany, 1° of hardness represents 1 part of $Ca\,O$ in 100,000 of water; in France, 1 part of $Ca\,C\,O_3$ in 100,000 of water; in England, 1 part of $Ca\,O$ in 70,000 of water. As the number of Cc. of soap solution used do not increase in exact proportion with the degrees of hardness, tables have been published by Faisst and Knauss to show the exact value of each reading of the burette, or the graduated instrument, called the *hydrotimeter*.

PREPARATION. While any good, white castile soap may be made to answer by standardizing its solution in methyl alcohol, it is generally preferred to make the soap solution by the decomposition of lead plaster by potassium carbonate; 150 parts of lead plaster are melted on a water bath and thoroughly mixed with 40 parts of pure potassium carbonate. The mixture is extracted by strong alcohol, filtered and the filtrate evaporated to dryness. Of this potash soap 20 gr. are dissolved in 1 litre of dilute 60% methyl alcohol of spec. gr. 0.9213 and then adjusted by dilution with ammonia water, so that 45 Cc. exactly correspond to 100 Cc. of barium chloride solution containing 0.523 gr. of $Ba\,Cl_2 + H_2O$ in 1 litre, and will represent 12 German degrees of hardness or 12 milligrammes of $Ca\,O$ in 100 Cc. of water. To make the test 100 Cc. of the water specimen are put into a capacious flask and soap solution added from the burette or hydrotimeter until permanent foam remains after shaking. The number of Cc. is read off, and, as the degrees vary in value according to the hardness of the water, the corresponding values in German degrees are obtained from

FAISST AND KNAUSS' TABLE.

Degrees Hardness.		Soap Solution.	Degrees Hardness.		Soap Solution.	Degrees Hardness.		Soap Solution.
0.5	=	3.4 Cc.	4.5	=	18.9 Cc.	8.5	=	33.3 Cc.
1.0	=	5.4 "	5.0	=	20.8 "	9.0	=	35.0 "
1.5	=	7.4 "	5.5	=	22.6 "	9.5	=	36.7 "
2.0	=	9.4 "	6.0	=	24.4 "	10.0	=	38.4 "
2.5	=	11.3 "	6.5	=	26.2 "	10.5	=	40.1 "
3.0	=	13.2 "	7.0	=	28.0 "	11.0	=	41.8 "
3.5	=	15.1 "	7.5	=	29.8 "	11.5	=	43.4 "
4.0	=	17.0 "	8.0	=	31.6 "	12.0	=	45.0 "

Of very hard water only 50 Cc. or even 25 Cc. are used and diluted to 100 Cc. and the degrees found multiplied accordingly.

SODIUM AND ITS COMPOUNDS.

NOTE. As stated in a note on potassium and its compounds, on page 150, it is in many analytical operations immaterial whether the salts of sodium or of potassium with the same acid are used, due allowance being made for the difference in atomic weight. Hence, the descriptions of uses, tests for purity and preparation to a great extent apply to sodium salts, as well as those of potassium, and need not be repeated. The tests for freedom from metallic impurities are the same for all sodium salts, and are, therefore, given with the metal at the start and only referred to briefly with the individual salts.

SODIUM, Na.

USES. Metallic sodium, on account of its great affinity for oxygen, iodine, chlorine, etc., removes them from their compounds, and by this and by the liberation of hydrogen it acts as a strong reducent and is much employed in organic work. For such purpose it is used either alone or, where a slower continuous action is desirable, as amalgam, with more or less excess of mercury. With acids it serves to convert arsenic into $As\,H_3$, and thus lead to its detection. It is used in the preparation of aluminum and magnesium, and for that purpose is now manufactured on a large scale. In connection with di-azo-benzol-sulphonic acid it serves to detect aldehydes, glucose, etc., by a red color (*Fischer and Penzold*). See Sulphanilic Acid, page 20. Na = 22.998.

TESTS. Pure metallic sodium has a silvery lustre; it may be crystallized in regular octohedra; spec. gr. 0.972; melts at 95.6° C. To prevent its oxidation it must be preserved under a cover of

petroleum naphtha or paraffin, or enclosed in an atmosphere of hydrogen. Perfectly dry chlorine or bromine does not affect it in the cold. Its solution in hydrochlyric acid must not give color or precipitate with H_2S, nor after addition of ammonia with ammonium sulphide or carbonate, nor with sodium phosphate. The solution in HCl must yield no ammonia vapor when heated with caustic lime, nor deposit a yellow precipitate on addition of sodio-cobaltic nitrite, even after long standing; its spectrum must show the D line unaccompanied by potassium or lithium lines. *These tests must be given by all the salts of sodium when perfectly free from metallic impurities.*

PREPARATION. In an iron retort, with suitable condenser, an intimate mixture of 30 parts of dry sodium carbonate, 13 parts of lampblack or fine coke powder and 5 parts of calcium carbonate, is heated to a bright red heat, and the distilling metal condensed under petroleum naphtha or melted paraffin. If necessary, it is purified by redistillation.

Sodium amalgam is made by melting together, under a cover of paraffin, 1 part of sodium with 50 parts of mercury. The molecular proportion (46 to 200) is therein deviated from by adding more mercury as a diluent, to prevent too vigorous reaction.

SODIUM ACETATE, $NaC_2H_3O_2 + 3H_2O$.

USES. For detection of alcohol as ethyl acetate by heating it with sodium acetate and sulphuric acid. For the precipitation of ferric salts as insoluble basic acetate. For the removal of phosphoric acid, ferric or aluminium phosphate, dissolved in hydrochloric acid becoming insoluble on heating with sodium acetate solution. It is also used as an addition to uranium solution in volumetric determination of phosphoric acid. It is also used in separating the bases of the third and fourth analytical group (those precipitated by ammonium sulphide), ferric and aluminium salts being precipitated by boiling with sodium acetate as basic acetates, while manganese and zinc salts remain in solution. Also to detect arsenic by the production of Kakodyl. Also for the preparation of pure acetic acid. A solution of 10 gr. of tannic acid and 10 gr. of sodium acetate in 100 Cc. of water is used under the name of *tannin reactive* for the separation of *basic* from *acid* coaltar dyes. The basic colors, such as fuchsine, malachite green, phosphine, flavaniline, methylene blue, methyl violet, bismarck brown, etc., are precipitated from aqueous solution by the addition of a small amount of the reagent and heating, while acid colors, such as the phthaleïns, rosaniline sulphonic

acid, azocolors, alizarin, etc., remain unaffected (*Weingaertner*). $Na\ C_2 H_3 O_2 + 3H_2 O = 135.746$.

TESTS. Sodium acetate forms colorless monoclinic crystals, which effloresce in dry, warm air. At 15° C. it dissolves in about 3.5 parts of water; at 100°, in 0.5; in absolute alcohol it is insoluble, but somewhat soluble in dilute, in 48 parts of 90%. At 58° C. it melts, and at 123° it boils. Its solution must satisfy the tests for absence of other metals, as directed for metallic sodium. It should not effervesce with acids, nor be rendered turbid by barium chloride, nor dilute solution of silver nitrate, nor should it give the nitric acid reactions with di-phenyl-amine or pyrogallol and sulphuric acid. When brought together with conc. sulphuric acid the dry salt should give neither color nor empyreumatic odor.

PREPARATION. Pure acetic acid is accurately neutralized by pure sodium carbonate and crystallized. The test solution contains 1 part in 10 parts of water; it does not keep well, on account of mould.

SODIUM ARSENATE, $Na_2\ H\ As\ O_4 + 7\ H_2 O$, is recommended by *Vitali* to identify morphine. A solution of morphine in concentrated sulphuric acid, on heating with a little sodium arsenate, becomes first blue, then green, then, on dilution with water, changes to rose-red and, finally, to blue. Addition of ammonia in excess turns the color green. The commercial salt is sufficiently pure.

SODIUM BROMATE, $Na\ Br\ O_3$.

USES. Like those of potassium bromate, to liberate, in connection with H Cl or other acids, iodine from iodide, bromine from bromide; hence, for titration of phenol, according to *Koppeschaar*. $Na\ Br\ O_3 = 150.646$.

TESTS. Sodium bromate forms shining tetrahedra, soluble at 15° C. in 8 parts of water. The same tests are applicable to it as for metallic sodium and for potassium bromate. See page 152.

PREPARATION. Hot conc. solution of sodium hydrate is saturated with bromine and the crystals, which separate on cooling of the evaporated solution, are purified by recrystallization.

SODIUM CARBONATE.

a. NEUTRAL SODIUM CARBONATE, $Na_2\ C\ O_3 + 10\ H_2\ O$.

USES. Sodium carbonate is used for the same purposes as potassium carbonate, neutralization of acids, precipitation of me-

tallic bases, and transfer of the acids of their salts to the sodium for easier examination. In blowpipe analysis the anhydrous salt, Na_2CO_3, is employed to reduce metals, to convert sulphates into sodium sulphide (hepar), etc. Also for fluxing silicates, titanates, etc., for which a mixture of 6.5 parts of potassium carbonate and 5.3 parts of the dry sodium salt is mostly preferred on account of the mixture melting at a lower temperature than either salt unmixed (see potassium carbonate, page 154). Also for detection of manganese, which fuses with Na_2CO_3 to form blue-green manganate. $Na_2CO_3 = 105.67$; $Na_2CO_3 + 10 H_2O = 285.27$.

TESTS. $Na_2CO_3 + 10 H_2O$ crystallizes in colorless monoclinic prisms, which in dry air rapidly lose water and at 100° C. become anhydrous. The crystals dissolve in 1.6 parts of water at 15°, in 0.185 parts at 100° C. The anhydrous salt at 15° C. dissolves in 6.7 parts, at 100° in 2.3 parts. In alcohol it is insoluble. The tests for metallic impurities are those directed for metallic sodium, page 181; those for acids the same as for potassium carbonate, page 154.

PREPARATION. The purest commercial dicarbonate (bicarbonate), such as made from kryolite, is placed into a glass funnel or percolator, and small quantities of pure water are, from time to time, sprinkled upon it until the solution dripping from it no longer gives a brown red precipitate with mercuric chloride, and, after acidulation with nitric acid, ceases to be rendered turbid by barium chloride and by silver nitrate. The salt is then dried and heated in a silver dish to a temperature of 150° C. to 180° C, so as to expel CO_2 and H_2O. A red heat must be avoided to prevent the formation of Na O H, which is copiously formed at 400° C.

The test solution is made to contain 20% of the anhydrous salt.

b. ACID SODIUM CARBONATE, $NaHCO_3$.

(*Di or Bi-carbonate.*)

USES. For similar purposes as the potassium salt. It is recommended by *Holthoff* for fluxing silicates, etc., in preference to the mixed carbonates of potassium and sodium, or either neutral carbonate alone on account of its promptness of decomposing the minerals at a lower temperature. $NaHCO_3 = 83.852$.

TESTS. Pure sodium dicarbonate can be obtained in monoclinic prisms, but is usually met with in form of powder. It dissolves in about 10.5 parts of water at 15° C.; at higher temperature it loses CO_2 and is gradually converted into neutral carbonate. In addition to the tests for purity, as directed for the carbonate, it should, for some purposes, be free from neutral carbonate formed by exposure to heat, and, therefore, must not give a brown-red

precipitate with mercuric chloride, which indicates presence of Na_2CO_3. For most purposes the product prepared from kryolite (e. g., that of the Pennsylvania Salt Co., at Natrona) is sufficiently pure.

PREPARATION. Commercial dicarbonate is purified by packing into a percolator and washing repeatedly with small portions of pure water until the drippings no longer produce a brown-red precipitate with mercuric chloride, nor after acidulation by nitric acid are rendered turbid by silver nitrate or barium chloride. It is then very carefully dried at a low temperature.

SODIUM CHLORIDE, Na Cl.

USES. For the precipitation of lead, silver and mercurous salts. In volumetric solution for the wet assay of silver and as companion solution to silver nitrate in various precipitation analyses. In conc. solution as a precipitant of bebeerine (*Bachmeyer*). As a precipitant of albumen in urine, *Roberts* recommends a solution of one part Na Cl in 2.5 parts of water containing 5% of hydrochloric acid of spec. gr. 1.052. In the so-called *halimetric method* of analysis of beer it serves to determine the CO_2 expelled by shaking the beer with sodium chloride by the difference in weight before and after the operation. It also serves for preparation of hydrochloric acid and chlorine and for furnishing monochromatic light for the polariscope. $NaCl = 58.368$.

TESTS. Sodium chloride crystallizes in transparent, colorless cubes, soluble at 14° C. in 2.79 parts of water, at 100° in 2.52 parts; very sparingly in alcohol. At 772° C. it melts, and if it then comes in contact with the flame it loses Cl and becomes partly converted into carbonate; hence, great care must be observed in its fusion. It reacts neutral to testpaper, and when pure is not deliquescent. It should stand the same tests for absence of other metals as are directed for metallic sodium, page 181. With silver nitrate it should yield a pure white precipitate, soluble without residue in dilute ammonia water. After addition of chlorine water, or dilute nitrous acid, it should give no color either to starch or to chloroform or ether shaken with it. After heating to dryness with hydrochloric acid, the residue must completely dissolve in water. No precipitate must be produced by barium chloride. The colorless transparent cubes of natural rock salt (sal gemmæ) are often found absolutely pure.

PREPARATION. When pure sal gemmæ is not obtainable, the best commercial salt may be purified by the method of *Margueritte*. Saturated solution of Na Cl in water is charged with H Cl gas, which causes the salt to separate in small crystals, which are

drained upon a funnel, washed with hydrochloric acid and then heated to expel the excess of acid.

Deci-normal solution contains 5.8368 gr. in 1 litre of water. It is either made by direct weighing of pure fused salt or by diluting a stronger solution so as to correspond with a solution containing in 1 litre 10.7675 of pure silver converted into nitrate. Potassium chromate generally serves as indicator.

SODIUM DIBORATE, $Na_2B_4O_7 + 10\,H_2O$.

Borax.

USES. Both the crystals, $Na_2B_4O_7 + 10\,H_2O$, and the fused an hydrous $Na_2B_4O_7$, the so-called borax glass are used. In blow-pipe work it serves to convert metallic compounds into borates, which dissolve in the fusing borax glass and are recognized by the color communicated to the bead and their behavior in different parts of the flame. For this purpose a small portion is fastened to a loop of platinum wire and heated in the oxidation flame until it melts into a colorless transparent globule of suitable size. To this while hot the specimen to be examined is attached and again placed into the flame for fusion. If powdered borax be mixed with glycerin and introduced into the flame the green color of boracic acid will flash up for an instant and thus detect both glycerin and borax. The alkaline reaction of borax is changed to acid by addition of poly-atomic alcohols (*Klein*, *Jehn*). In docimastic assaying borax is used as a flux to exclude air as well as to dissolve silica and other substances. $Na_2B_4O_7 = 201.48$; $Na_2B_4O_7 + 10\,H_2O = 381.08$.

TESTS. The crystals of borax with 10 mol. of water are monoclinic prisms, soluble in 14 parts of water at 15°, in 0.5 parts at 100°. There are also hexagonal crystals, with 5 mol. of water, which separate from hot concentrated solution. When heated water escapes, puffing up the salt to a white, spongy mass, which at 561° C. melts to transparent, colorless *borax glass*. A good re-crystallized article of commercial borax is sufficiently pure. Its solution should give no precipitate with sodium carbonate, nor, after acidulating with nitric acid, become turbid by the addition of silver nitrate or barium chloride.

PREPARATION. The commercial salt is repeatedly recrystallized and either preserved in crystals or powder, or it is fused in a platinum vessel and powdered.

SODIUM HYDRATE, Na C H.

USES. For the same purposes as potassium hydrate, see page 162, for which it may be substituted in all cases where the introduction of sodium is not objectionable. For volumetric work sodium is less desirable than potassium hydrate on account of its troublesome foaming and greater liability to corrode glass. Na O H = 39.958.

TESTS. For metallic impurities the same as for metallic sodium, page 181; for other impurities the same as for potassium hydrate, page 162. It is soluble at 15° in 1.7 parts, at 100° in 0.67 parts of water, and quite soluble in alcohol. Exposed to air it first attracts moisture and then CO_2 and becomes covered with a crust of carbonate.

PREPARATION. From sodium carbonate and calcium hydrate or from sodium sulphate and barium hydrate, or from metallic sodium, in the same manner as directed for potassium hydrate. Ordinary test solution contains from 10 to 12%; normal solution, 39.958 grammes in 1 litre.

SODIUM HYPOCHLORITE SOLUTION, Na Cl O.

USES. As a source of chlorine; for oxidation of nickelous to nickelic salts, etc.; for solution of arsenic spots in Marsh's test, and their distinction from antimony spots, which do not dissolve. For liberation of nitrogen from urea instead of sodium hypobromite. For detection of aniline, with which it produces a violet-purple color; codeine dissolved in conc. sulphuric acid gives a blue, aesculin a violet color with sodium hypochlorite (*Raby*); morphine, dissolved in it and then neutralized with ammonia, assumes a dark red color (Fairthorne). The liquor sodæ chloratæ of the U. S. P. is sufficiently pure.

PREPARATION. 80 parts of bleaching powder (impure calcium hypochlorite) are diffused in 400 parts of water, and into this are poured 100 parts of sodium carbonate dissolved in 400 parts of boiling water. After cooling, enough water is added to make 1,000 parts. Strain and preserve the clear liquid in well stopped bottles.

SODIUM HYPOBROMITE SOLUTION, Na Br O.

USES. For the determination of ammonia and urea by the method of *Knop and Huefner*. A freshly prepared solution of hypobromite is added to the ammonia or urea in a suitable apparatus, which permits the measuring of the nitrogen liberated by the decomposition:

$$2\,NH_3 + 3\,NaBrO = 3\,NaBr + 3\,H_2O + N_2;$$

$$CO(NH_2)_2 + 3\,NaBrO = 3\,NaBr + 2\,H_2O + CO_2 + N_2.$$

1 gr. urea contains 0.46666 gr. N, which at a pressure of 760 Mm and

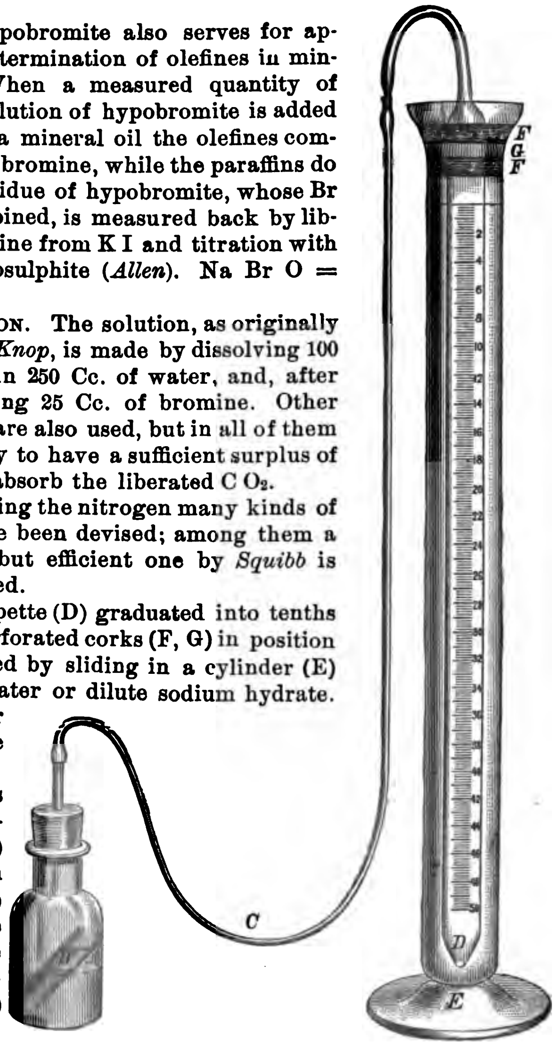
0° C. occupies 372.7 Cc., so that each 1 Cc. of nitrogen corresponds to 0.002681 gr. of urea. Or a volumetric solution of hypobromite is added in excess to the urea and the surplus after decomposition is measured back (*Hamburger*). As it requires 3 mol. of hypobromite (Na Br. O = 118.726) to decompose 1 mol. of urea ($C\,O\,N_2\,H_4$ = 59.976), each 1 gr. of bromine used corresponds to 0.213 gr. of urea.

Sodium hypobromite also serves for approximate determination of olefines in mineral oils. When a measured quantity of volumetric solution of hypobromite is added in excess to a mineral oil the olefines combine with the bromine, while the paraffins do not. The residue of hypobromite, whose Br has not combined, is measured back by liberation of iodine from K I and titration with sodium hyposulphite (*Allen*). Na Br O = 118.726.

PREPARATION. The solution, as originally directed by *Knop*, is made by dissolving 100 gr. Na O H in 250 Cc. of water, and, after cooling, adding 25 Cc. of bromine. Other proportions are also used, but in all of them it is neceseary to have a sufficient surplus of Na O H to absorb the liberated $C\,O_2$.

For measuring the nitrogen many kinds of appaatus have been devised; among them a very simple but efficient one by *Squibb* is here illustrated.

A 50 Cc. pipette (D) graduated into tenths is held by perforated corks (F, G) in position easily changed by sliding in a cylinder (E) filled with water or dilute sodium hydrate. The upper tube of the pipette is bent and by means of a long rubber tube (C) connects with the bottle (A) containing the hypobromite and in a separate tube (B) 4 Cc. of urine.



Allen's volumetric solution for olefines contains 40 Cc. of bromine and sufficient sodium hydrate to make the solution feebly alkaline in 1 litre. Its titre is ascertained by the iodine liberated from K I, measured by deci-normal sodium hyposulphite.

SODIUM HYDROSULPHITE SOLUTION, $Na_2 S_2 O_2$,

Is recommended by *Schuetzenberger* and *Risler* (under the title hyposulphite) for the titration of oxygen in water, sodium sulphindigotate serving as indicator.

The solution is prepared by shaking a solution of sodium acid sulphite of spec. gr. 1.25 with a surplus of zinc dust, diluting with 10 parts of water from which the air has been expelled by boiling, adding milk of lime to alkaline reaction and drawing off the clear liquid without permitting access of air (*Tiemann and Preusse*). The titre is adjusted by an ammoniacal solution of 4.469 gr. of cupric sulphate in 1 litre. 10 Cc. of this solution correspond to 0.001434 gr. of Cu_2 O, equal to a loss by reduction of 1 Cc. oxygen at 0° and 760 Mn. barometric pressure. A measured quantity of the water to be examined is added to sodium sulphindigotate, which by addition of sodium hydrosulphite has just been deprived of its blue color. Shaking with the oxygen of the water restores the blue color, which is again dispersed by titration with the hydrosulphite, and thus the contents of oxygen determined. In alkaline solution it serves to detect anthraquinone by a red color. It is to be regretted that the name *hyposulphite*, properly belonging to the salt $Na_2 S_2 O_3$, has been applied to the *hydrosulphite*, $Na_2 S_2 O_2$, while $Na_2 S_2 O_3$ is now often called *thiosulphate*, thus giving rise to mistakes.

SODIUM HYPOSULPHITE, $Na_2 S_2 O_3 + 5 H_2O$.

Sodium Thiosulphate.

USES. In deci-normal solution as a companion to iodine in the various operations of iodimetry; for titration of free iodine and of all substances capable of liberating it from potassium iodide; for solution of silver salts; in blow-pipe analysis for detection of cyanides. A bead of hyposulphite is charged with the supposed cyanide, and, while hot, dipped into dilute solution of ferric chloride. A red color, due to the formation of ferric sulphocyanide, reveals the presence of cyanide (*Froehde*). $Na_2 S_2 O_3 + 5 H_2 O = 247.644$.

TESTS. Sodium hyposulphite crystallizes in colorless, transparent monoclinic prisms, soluble at 15° in 0.65 parts of water, insoluble in alcohol. At 56° C. it melts and at 100° becomes anhydrous, at 225° it is decomposed. The same tests for metallic impurities

apply as directed for metallic sodium; but an absolutely pure salt is rarely needed. It should not effervesce with acetic acid; a 1% solution should not be rendered turbid by barium chloride; no red color should be communicated to phenolphthalein. To show absence of chlorine the salt must first be converted into sulphate, either by sulphuric acid or by hydrogen dioxide, the filtered solution must not be rendered turbid by silver nitrate. Very pure salt is now sold by dealers in photographic goods.

PREPARATION. The salt obtained on a large scale, as a bye-product of the Leblanc soda process, may be purified by repeated recrystallization. Or sodium sulphite is boiled with excess of sulphur, filtered and crystallized.

Deci-normal solution contains 24.7644 gr. in 1 litre, but, on account of the varying amount of water in the salt, it is best prepared, not by direct weighing, but by adjusting a stronger solution by deci-normal iodine (containing 12.6557 gr. in 1 litre). The solution should be made with water from which all oxygen has been expelled by boiling and carefully preserved in the dark.

SODIUM IODATE, $Na\,I\,O_3$.

USES. This salt is occasionally used instead of potassium iodate to make iodic acid for alkaloid analysis. It is prepared in the same manner as the potassium salt, see page 164. $Na\,I\,O_3 = 197.435$.

SODIUM MOLYBDATE, $Na_2\,Mo\,O_4 + 2\,H_2O$, is occasionally used instead of molybdic acid, or ammonium molybdate, for preparation of Froehde's reagent, etc. It is made by saturating molybdic acid with sodium hydrate. See *Molybdic Acid and derivatives*, pp. 12 and 13

SODIUM NITRATE, $Na\,N\,O_3$.

USES. It is used for the same purpose as the potassium salt, for which it is substituted when it is not desirable to introduce potassium. $Na\,N\,O_3 = 84.899$.

TESTS. Sodium nitrate crystallizes in the hexagonal system, forming colorless rhombohedra. At 15° C. it dissolves in 1.25 parts of water, at 100° in 0.56 parts. It is to be tested especially for freedom from iodine, chlorine, sulphate and phosphate, calcium and magnesium. Tests are the same as directed for sodium metal and for potassium nitrate.

PREPARATION. On the large scale, by refining Chili saltpetre by recrystallization; in small quantity by saturating nitric acid with sodium carbonate and crystallizing.

SODIUM NITRITE, $Na\,N\,O_2$.

USES. For the same purposes as the potassium salt, except for the separation of cobalt, in which potassium is required; hence, it serves for conversion of amines into di-azo compounds, for recognition of phenols, of antipyrine, for liberation of iodine, etc. Also in the preparation of sodio-cobaltic nitrite, the reagent for potassium (*Curtman*), see page 75. $Na\,N\,O_2 = 68.939$.

TESTS. The salt crystallizes in colorless rhombohedra, but is generally sold fused in pencils. It is very soluble in water and in alcohol. The tests for purity of metallic sodium and of potassium nitrite apply to sodium nitrite.

PREPARATION. By fusion of sodium nitrate with lead in the same manner as the potassium salt.

SODIUM NITROPRUSSIDE, $Na_2\,Fe\,(N\,O)\,C_5\,N_5 + 2\,H_2O$.

USES. For the detection of alkaline sulphides, which, even in traces, give with solution of nitroprusside a red purple color, which rapidly changes to deep blue. Alkaline hyposulphites do not give the reaction while unchanged, but by heating they are decomposed, and the formation of sulphide is then shown by the above reaction. Sulphites in neutral or alkaline solution give a deep red with a mixture of nitroprusside and zinc sulphate (*Boedeker*). After addition of sodium carbonate to the solution of nitroprusside it serves to detect creatinine in urine by an intense red color, which gradually turns to straw yellow, the change being hastened by acidulating with acetic acid (Weyl). Acetone, under like treatment, becomes brown red, and on acidulation turns purple (*Legal*). Sodium nitroprusside precipitates many alkaloids, whose characteristic crystalline forms serve to distinguish them under the microscope (*Davy*). It is also used in the differentiation of oils. Mol. W. = 297.785.

TESTS. Sodium nitroprusside crystallizes in ruby red, rhombic prisms, soluble in 2.5 parts of water at 15°, insoluble in alcohol; the solution is decomposed by boiling heat and by direct sunlight. The salt need not be absolutely pure, but must give the reaction with sulphides even in the minutest traces.

PREPARATION. Four parts of powdered potassium ferrocyanide are heated with 5.5 parts of nitric acid, of spec. gr. 1.2, until the solution no longer gives a blue color with ferrous sulphate. On cooling, potassium nitrate crystallizes out and is removed; the solution is concentrated again and the nitrate removed on cooling, the last portion may be precipitated by addition of alcohol. The nitroprussic acid is then saturated with sodium carbon-

ate, the solution concentrated and the deep red crystals separated and purified by recrystallization.

SODIUM OXALATE, $Na_2 C_2 O_4$

USES. In volumetric analysis of superphosphates to remove the calcium as insoluble oxalate and unite the phosphoric acid to sodium, without disturbing the relative proportions of acid and base (*Mollenda*).

TESTS. The salt is generally obtained as a crystalline powder, soluble in 31.3 parts of water at 15° C. and in 15.8 parts at 100°. If wanted perfectly pure it should give the tests directed for metallic sodium and for potassium oxalate; but this is hardly necessary, the main requirement is perfect neutrality.

PREPARATION. A saturated hot solution of oxalic acid is accurately neutralized with sodium carbonate or hydrate, and the resulting salt carefully dried.

SODIUM PHOSPHATE, $Na_2 H P O_4 + 12 H_2 O$.

USES. Secondary sodium *ortho-phosphate*, $Na_2 H P O_4$, is used to precipitate many metals, forming phosphates insoluble in water. After separation of the metals of groups III, IV, V and VI by means of $H_2 S$ and $(N H_4)_2 S$, it is employed to precipitate Ba, Sr, Ca and Mg together, or, after Ba, Sr and Ca have been precipitated as carbonates, while Mg was held in solution by ammonium chloride, to detect and precipitate magnesium as $Mg N H_4 P O_4$. In conjunction with sodium acetate it serves for precipitation of chromic salts as chromic phosphate (*Carnot*), of cadmium (*Carnot and Proromont*), so as to prepare them for weighing. It is also used for precipitation of zinc in neutral solution and its separation from magnesium, which only precipitates from solution made alkaline by ammonia (*Loeseman and Meyer*). $Na_2 H P O_4 = 141.794$; $Na_2 H P O_4 + 10 H_2 O = 357.314$.

TESTS. $Na_2 H P O_4 + 10 H_2 O$ crystallizes in colorless, monoclinic prisms, which lose water in air. It dissolves at 15° C. in 10.4, at 30° in 2.5, at 40° in 0.95 and at 99° in 0.611 parts of water. At 35° it melts, becomes anhydrous at 100°, and at 300° is converted into pyrophosphate, $2 Na_2 H P O_4 = Na_4 P_2 O_7 + H_2 O$. The solution must not effervesce with acids, must yield no precipitate with ammonium carbonate, hydrate, oxalate or sulphide, the precipitates made by silver nitrate or barium chloride must completely redissolve on addition of nitric acid. After heating to dryness with H Cl no insoluble residue must be left on addition of water. Absence of arsenic must be shown.

PREPARATION. On the large scale, it is made by digesting bone ashes with dilute sulphuric acid, separating the calcium sulphate by filtering and concentration, then adding sodium carbonate to alkaline reaction. The filtrate is concentrated, and the crystals obtained on cooling are purified by recrystallization. On the small scale sodium carbonate is added to phosphoric acid until the reaction becomes alkaline and crystals obtained as above. The ordinary test solution contains 10% of the salt.

SODIUM AMMONIUM PHOSPHATE, $Na(NH_4)HPO_4 + 4H_2O$.

Microcosmic Salt.

USES. This salt is easily converted by heat into sodium *metaphosphate*, $NaPO_3$, and, therefore, is very useful in blowpipe work for detecting metals by the color of their beads, which give clearer and more characteristic reactions than those with borax, but being much more fusible require a much narrower platinum loop to keep them from dropping off. Silica leaves an insoluble skeleton of the shape of the mineral fragment containing it, and is, therefore, easily observed in the transparent bead. As the salt is not so liable to lose water of crystallization as the sodium phosphate, it is used for making, by direct weighing, solutions for standardizing uranium solution used in titration of phosphoric acid. Instead of making them deci-normal (containing 20.8657 gr. in 1 litre) an empirical solution is often employed containing 29.339 gr. in 1 litre, corresponding to 10 gr. of phosphoric anhydride, P_2O_5. The salt is also used for precipitation of magnesium and other purposes, instead of the sodium phosphate. $Na(NH_4)HPO_4 = 136.817$; $Na(NH_4)HPO_4 + 4H_2O = 208.657$.

TESTS. Microcosmic salt forms colorless, monoclinic crystals, soluble in about 4.5 parts of water at 15°, much more soluble in boiling water. The same tests for purity apply as for sodium phosphate. When heated on platinum foil or wire it must give a perfectly transparent mass.

PREPARATION. Six parts of sodium phosphate and 1 part of ammonium chloride are dissolved in 2 parts of boiling water, and after a short time of heating together are set aside to cool. The double salt separates in crystals and is recrystallized from water containing a little ammonia, so as to purify them from adhering $NaCl$.

SODIUM PYROPHOSPHATE, $Na_4P_2O_7 + 10H_2O$, is used in electrolytic separations of nickel, cobalt, iron, manganese, zinc, cadmium, copper, silver, mercury, etc. The pyrophosphates of these

metals are precipitated from solution by the sodium pyrophosphate, add are redissolved as double salts when the sodium salt is added in sufficient excess. By adding either ammonium hydrate, or carbonate, or oxalate, or various other substances, to the solution, it is possible to precipitate some of the metals by the electric current, leaving others in solution (*Brand*). The salt is prepared by heating to redness pure secondary orthophosphate, dissolving and crystallizing the residue. It forms large, transparent monoclinic prisms, soluble in ten parts of cold and 1 part of boiling water.

Sodium phospho-tungstate, see *phospho-tungstic acid*, page 18.

SODIUM SALICYLATE, $2 Na C_7 H_5 O_3 + H_2 O$, is proposed by *Hager* as a reagent to test the purity of quinine sulphate. To a saturated solution of quinine sulphate in water a few drops of 20% solution of sodium salicylate are added. If the quinine was pure the solution remains clear; cloudiness indicates presence of other cinchona alkaloids. It also serves to detect ethyl - and especially methyl - alcohol, by heating with a small amount of the salicylate and concentrated sulphuric acid, when it gives the odor of gaultheria. See also on page 88.

SODIUM SELENATE, $Na_2 Se O_4 + 10 H_2 O$, is proposed by *Johannson* for detection of colocynthin, which is colored reddish-yellow in contact with a solution of sodium selenate in dilute sulphuric acid. Also used for demonstrating brucine in microscopical sections of strychnos seeds by using it dissolved in nitric acid (*Lindt*). The commercial product is sufficiently pure.

SODIUM SULPHANTIMONATE, $Na_3 Sb S_4 + 9 H_2 O$.

Schlippe's Salt.

USES. For precipitation of quinine, morphine and other alkaloids, as sulphantimonates of yellow to brownish color, differing as to formation of resinous masses, solubility in excess of precipitant, etc. Dilute aqueous solutions are used, sometimes with the addition of alcohol (*Palm*). Mol. W. = 478.525.

TESTS. Sodium sulphantimonate crystallizes in orange red, transparent, regular tetrahedra, which, by long keeping, become superficially coated with opaque, orange yellow $Sb_2 S_5$. The salt is soluble in 3 parts of water at 17°; in 1 part at 100°. Clear, transparent crystals are sufficiently pure for use.

PREPARATION. 21 parts of finely powdered gray antimonous sulphide, $Sb_2 S_3$, 2 parts of sulphur and 30 parts of sodium hydrate are boiled with 180 parts of water until the gray color has disappeared, filtered and concentrated. A little alcohol is then added

and the liquid set aside to crystallize. The pure crystals are selected, washed with alcohol and then carefully preserved without removing the adhering alcohol. This prevents their decomposition for a long time.

SODIUM ACID SULPHATE, $Na\ H\ S\ O_4$.

USES. Instead of potassium disulphate as a flux for decomposing and rendering soluble aluminium minerals, such as emery, corundum, which are insoluble in acids, and for which the use of potassium salt would lead to troublesome formation of alum. (*J. Lawrence Smith.*)

TESTS. The fused mass or the anhydrous triclinic prisms are to be tested like the corresponding potassium salt.

PREPARATION. 15 parts of pure crystallized sodium sulphate, $Na_2\ S\ O_4 + 10\ H_2\ O$, and 5 parts of conc. sulphuric acid are heated in a platinum vessel until all of the water has escaped and white fumes of sulphuric acid begin to form, while the mass is in quiet fusion. On cooling it is broken into small pieces and preserved.

SODIUM SULPHIDE SOLUTION, $Na_2\ S$.

USES. In docimastic assaying for titration of zinc and nickel; alkaline solution of lead, or alkaline solution of iron in glycerin, nickel chloride, or cobalt paper being used as indicators by spotting. $Na_2\ S = 77.98$.

PREPARATION. 13 gr. of sodium hydrate are dissolved in water to make one litre. 500 Cc. are then saturated with $H_2\ S$ and, after expelling the surplus by gentle heat, are mixed with the rest of the solution. This now contains somewhat more than the 12.01 gr. of $Na_2\ S$ necessary to convert 10 gr. of zinc into sulphide. It is therefore standardized by solution of 1 gr. of pure zinc, which, after solution in acid and neutralization by ammonia, must require exactly 100 Cc. of the sulphide solution. The adjusted solution is filled into small vials, nearly full, stopped with rubber and preserved, mouth downward.

SODIUM SULPHITE, $Na_2\ S\ O_3 + 7\ H_2\ O$.

USES. This salt serves occasionally as a reducent by introducing $S\ O_2$ into solutions. Also for the detection of arsenic. A small crystal of 0.01 to 0.02 gr. of $Na_2\ S\ O_3$ is thrown in a solution of 0.3 to 0.4 gr. of stannous chloride in 3 to 4 Cc. of pure conc. hydrochloric acid and the specimen to be tested for arsenic dissolved in hydrochloric acid is poured upon it to form a separate layer above it. If arsenic be present yellow $As_2\ S_3$ will form above the line of contact, by the $H_2\ S$ being liberated from $Na_2\ S\ O_3$ by the

reducing power of the stannous chloride (*Schlickum*). In concentrated solution, to which a little pyrogallol has been added, it serves to detect small traces of cupric salts by a blood red color (*Aliame*). $Na_2SO_3 = 125.86$; $Na_2SO_3 + 7H_2O = 251.58$.

TESTS. Sodium sulphite crystallizes in monoclinic prisms containing 7 mol. of water. It dissolves in about 2 parts of cold water; on heating a saturated solution anhydrous salt separates. In alcohol it is insoluble. By careless keeping it changes to sulphate. For making the tests above stated, the only requirement is that it should evolve, on addition of acids, a copious amount of SO_2.

PREPARATION. A saturated solution of sodium carbonate is divided into 2 equal portions. One of them is saturated with sulphur dioxide, forming *acid sulphite*, and then the other portion added and crystals obtained.

Sodium acid sulphite is sometimes used to separate *acetone*, which forms with it a crystallized compound $C_3H_6O.NaHSO_3$, from which acetone may be again obtained by heating with sodium hydrate.

SODIUM TARTRATE.

a. ACID SODIUM TARTRATE, $NaHC_4H_4O_6 + H_2O$.

USES. In freshly prepared saturated solution for precipitation of potassium (ammonium and calcium) as acid tartrate. Also for preventing the precipitation of alumina, ferric oxide, etc. Mol. W. = 199.614.

TESTS. The salt crystallizes in rhombic needles, very soluble in water. The solution rapidly spoils by fungous growths. After ignition the solution of the residue should contain pure sodium carbonate.

PREPARATION. A saturated solution of tartaric acid in hot water is divided into two equal parts. One-half is accurately neutralized by sodium carbonate, to form neutral tartrate, and the other half is added and crystals obtained. The solution is only made immediately before use, and should be very concentrated.

b. NEUTRAL SODIUM TARTRATE, $Na_2C_4H_4O_6 + 2H_2O$.

USED for preparing Fehling's and Nylander's solutions, in the place of Rochelle salt, to aid in the solution of the metallic salts; the tests are the same as for the acid salt, and its preparation is there described.

c. SODIUM POTASSIUM TARTRATE, $NaKC_4H_4O_6 + 4H_2O$.

Rochelle Salt.

USED, as the preceding, in the preparation of Fehling's and Nylander's solution, etc. The pure salt forms colorless, transparent,

rhombic prisms, soluble in 1.7 parts of water at 6° C. After ignition its solution should only contain potassium and sodium carbonate. The commercial salt is sufficiently pure after recrystallization.

Sodium thiosulphate, see *sodium hyposulphite*, page 189.

SODIUM TUNGSTATE.

a. NEUTRAL TUNGSTATE, $Na_2 W\ \ _4 + 2 H_2 O$.

b. ACID TUNGSTATE, $Na_{10} W_{12} O_{41} + 28 H_2 O$ ($= 5 Na_2 W O_4 + 7 W O_3$), the ordinary commercial salt.

USES. Both salts serve as precipitants of albuminoids in urine, also for precipitating barium from solutions of its salts in strong acetic acid (Ca and Mg are precipitated only from neutral and alkaline solution). The salts also serve for the preparation of metatungstate and of phospho-tungstic and silico-tungstic acids, see page 18 and 19.

TESTS. The neutral salts form colorless, monoclinic prisms; the acid, triclinic. Both salts are quite soluble in water. They should be free from carbonate, sulphate and chloride. A solution in 20 parts of water should not effervesce with strong nitric acid, and after boiling the mixture, the filtrate should not give a precipitate with either silver nitrate or barium nitrate.

PREPARATION. Wolframite, a native tungstate of iron and manganese, is finely powdered and heated to bright redness after mixing with two-thirds of its weight of sodium carbonate. The mass is leached out by boiling water, and the hot solution poured into an excess of hot conc. nitric acid. A yellow precipitate of $W O_3$ falls. This is separated, washed and boiled with sodium carbonate. From this solution the neutral salt crystallizes. By neutralizing a hot, concentrated solution of this salt (or, on the large scale, the solution of the fused mass above obtained) with hydrochloric acid the acid salt is prepared and obtained in crystals.

When to the boiling, saturated solution of either salt some of the yellow $W O_3$ is added in small successive portions, so long as it loses its yellow color, the filtrate on evaporation yields metatungstate.

c. SODIUM META-TUNGSTATE, $Na_2 W_4 O_{13} + 10 H_2 O$ ($= Na_2 W O_4 + 3 W O_3$).

USES. For analysis of alkaloids, which it precipitates even in very small quantities, e. g., strychnine 0.0001 milligr. (*Scheibler*). It is tested as the salts above described.

STARCH.

USES. With free iodine starch forms a compound of such intense dark blue color that it remains visible even after the utmost dilution; bromine gives an intense yellow. Hence, starch is used to detect free iodine and bromine. Most varieties of starch give the blue color with iodine in the raw state, but a few varieties give a yellow or brownish color which might be mistaken for the bromine reaction. After boiling with water all varieties give the blue color with iodine, but after keeping for some time the color becomes uncertain again. Hence, the importance of a well keeping preparation of starch to be available at any time. Such solutions may be made by the aid of sodium, calcium or zinc chloride, by alkaline hydrate, etc. It is also important to have permanent starch solutions containing soluble iodides, from which small traces of chlorine, bromine or nitrous acid can liberate free iodine, and are thus instantly detected, and measured by titration with sodium hyposulphite (thiosulphate). Presence of alkaline, magnesium and aluminium sulphates, of albumin, resorcin, phloroglucin and other organic substances interfere with the promptness of the starch reactions.

PREPARATION. Starch solutions must be made thin and uniform without lumps. For ordinary purposes, 1 part of starch is thoroughly mixed with 10 parts of cold water, and then enough boiling water added, with constant stirring, to make about 200 parts of transparent jelly. To render this less liable to spoil, about 5% of calcium or zinc chloride may be added, or sodium chloride to saturation. A still better keeping solution is made, according to *Mueller*, by triturating 2 gr. of starch with 25 Cc. of conc. alkaline hydrate solution (which converts the cellulose of the starch into soluble granulose) until it becomes transparent, and then diluting with water to one litre. The alkali must be neutralized before using.

Soluble iodides are often added, especially $K\,I$, $Zn\,I_2$ and $Cd\,I_2$, to the preceding solutions to the amount of 0.5 to 1%. *Gastine* recommends that 5 gr. starch and 0.1 gr. of mercuric iodide be triturated with water, and then poured into enough boiling water to make one litre. The solution after filtering keeps for years.

STRONTIUM CHLORIDE, $Sr\,Cl_2 + 6\,H_2\,O$.

USES. In the volumetric determination of sulphates. They are precipitated by strontium chloride, the resulting almost insoluble strontium sulphate is converted into carbonate by boiling with

sodium carbonate, and the strontium carbonate is finally decomposed by a measured volume of normal hydrochloric acid and the surplus of acid measured back by normal alkali (*Mohr*). $Sr\ Cl_2 = 159.114$; $Sr\ Cl_2 + 6\ H_2O = 267.474$.

Tests. The salt forms hexagonal prisms, soluble at 15° C. in 0.75 parts of water and in 24 parts of absolute alcohol. For the use above described, it is sufficient that its solution give no precipitate with potassium dichromate (abs. of barium).

Preparation. Hydrochloric acid is saturated with strontium carbonate and the solution crystallized.

STRONTIUM SULPHATE, $Sr\ S\ O_4$.

Uses. In saturated aqueous solution for the detection of barium by precipitation as sulphate. Strontium sulphate requires about 3,500 parts of water for solution, and yields its acid to barium, which forms an insoluble sulphate. The solution is prepared by digesting pure, colorless, native coelestine (strontium sulphate) with water, or by preparing the strontium sulphate by precipitating its chloride or nitrate by dilute sulphuric acid, washing the precipitate thoroughly, and placing it in a large bottle filled with water, so as to obtain a saturated solution.

SUGAR, $C_{12}\ H_{22}\ O_{11}$.

Saccharose or Canesugar.

Uses. To detect small quantities of free sulphuric acid in vinegar, etc. The liquid, mixed with a small quantity of sugar, is evaporated in a porcelain dish on a water bath; a black or brown residue indicates free sulphuric acid (*Runge*). Also to detect bile acids by the deep red color they produce when mixed with sugar and conc. sulphuric acid (*Pettenkofer*). A reversal of this reaction is used to detect free sulphuric acid in alum, aluminium sulphate, etc. Bile (cholic acid) is mixed with sugar and the alum added; red color indicates free acid (*Egger*). The bile reactions depend on the formation of *furfurol* by the action of concentrated acid on sugar (*Mylius*). With morphine the mixture of sugar and sulphuric acid produces a violet color (*Tamba*). Free arsenic acid, $H_3\ As\ O_4$, mixed with sugar solution, assumes a rose red color after some hours, which, by longer standing, turns to deep purple. Milk sugar, glucose and mannite act similar to cane sugar; arsenates or arsenous acids do not give the reaction (*Fresenius' Zeitschrift*, xxi, 124). Commercial loaf sugar is sufficiently pure.

SULPHUR, S.

USES. For preparing sulphur dioxide, ferrous sulphide, sodium hyposulphite and other sulphur compounds. For combining with metals in some docimastic assays. For detection of bismuth by the production of the red iodide coating on charcoal, a mixture of sulphur and potassium iodide is added to the bismuth specimen and heated on charcoal before the blow pipe. S = 31.984.

TESTS. From solutions sulphur crystallizes in rhombic octohedra. It melts at 117° C., and from the state of fusion crystallizes in monoclinic prisms. At 447 it boils. The condensed vapor forms sublimed sulphur, the sulphur flowers of commerce, and this is the quality used as reagent for bismuth and for many preparations. Pure sulphur, to make pure preparations, must be completely volatilized by heat, must yield nothing to distilled water to disturb the neutrality of testpapers. It must be free from arsenic, which is detected by digesting with ammonia water, filtering and acidulating with hydrochloric acid. A yellow preeipitate of $As_2 O_3$ indicates arsenic. To detect selenium the sulphur is heated with nitromuriatic acid, diluted with water, and to the clear filtrate sodium sulphite is added, when a red precipitate indlcates the presence of selenium.

SULPHUR IODIDE.

An impure sulphur iodide, made by melting together 2 parts of iodine and 3 parts of sulphur, is used in blow pipe work to produce on plaster of paris tablets films of various metallic iodides (*Wheeler and Luedeking*).

SULPHUR TRIOXIDE, S O_3.

USES. In gas analysis, for the absorption of olefiant gas. The most concentrated (fuming) sulphuric acid obtainable is saturated with sulphur trioxide so as just to remain liquid. Into this solution little globes of coke are dipped and introduced into the absorption apparatus containing the dry mixture of gases (*Bunsen*). It is also used to rapidly concentrate sulphuric acid in *Kjelhahl's* process of nitrogen determination. Also for purposes of dehydration. S O_3 = 79.864.

TESTS. Sulphur trioxide forms long silky needles melting at 14.8° and boiling at 46.2°. When not entirely free from H_2 S O_4 a compound is formed, similar to asbestus in appearance, which does not boil at 50° C., but which at higher temperature decomposes and gives off vapors of pure trioxide. It fumes in air and attracts moisture, and must therefore be carefully preserved. It

is tested in the same way as sulphuric acid. See pages 21 and 105.

PREPARATION. By distillation, at a gentle heat, of fuming sulphuric acid, care being taken to cool the receiver well and to prevent absolutely all excess of moisture.

Tannin, see *Tannic Acid*, page 23.

Tannin-reagent for aniline dyes, see *Sodium Acetate*, page 182.

Testpapers, see Color Reagents, page 88.

THALLOUS NITRATE, $Tl\,N\,O_3$.

USES. For quantitative determination of iodine. In very dilute neutral solutions of chlorides, bromides and iodides a saturated aqueous solution of thallous nitrate precipitates the iodide as yellow thallous iodide, $Tl\,I$, which is totally insoluble in water while thallous chloride and bromide, though difficultly soluble, remain in solution (*Huebner and Frerichs*). $Tl\,N\,O_3 = 265.616$.

TESTS. Thallous nitrate forms colorless rhombic prisms, soluble at 15° C. in about 10 parts of water, much more soluble at 100°. At 205° it melts and at higher temperature is decomposed. It colors the flame green and shows a single green line in its spectrum. Its neutral or acid solution should not be precipitated by hydrogen sulphide. Addition of ammonia water should leave the aqueous solution clear even after heating, and from this solution ammonium sulphide precipitates it as black $Tl_2\,S$. After complete precipitation the filtrate on evaporation should leave no permanent residue.

PREPARATION. Metallic thallium is dissolved in dilute nitric acid and crystallized.

To prepare METALLIC THALLIUM the flue-dust and deposit of the lead chambers of sulphuric acid manufactories using thalliferous pyrites is leached out by boiling water, filtered, concentrated and mixed with conc. hydrochloric acid, which precipitates thallous chloride, a curdy, white salt, requiring 360 parts of cold water for solution, and still less soluble in hydrochloric acid. The precipitate is separated and added in small portions, with constant stirring, to half of its weight of hot conc. sulphuric acid, and the mixture heated to expel excess of acid. The fused acid sulphate resulting is dissolved in about 100 parts of water and $H_2\,S$ passed through the solution to precipitate any lead, silver, mercury, bismuth, arsenic, antimony or selenium, which may have been derived from the pyrites. The filtrate, after expulsion of the excess of $H_2\,S$, is heated with ammonia water, to precipitate iron, alumina, etc., and is then concentrated to crystallize *thallous sulphate*, which separates in colorless, rhombic prisms,

From this, *metallic thallium* is precipitated by pure zinc or by electrolysis, from solution made alkaline by ammonia.

THALLIUM PAPER, made by dipping unsized paper into *thallous hydrate* solution, Tl O H, is used to indicate ozone, which turns it into brown thallic salt (*Boettger*). The solution of thallous hydrate is prepared by adding to the solution of thallous sulphate, obtained as above described, enough barium hydrate to remove the sulphuric acid. The paper has also been used as an indicator for sodium sulphide titration.

THYMOL, $C_6 H_3 . C_3 H_7 . C H_3 . O H$.

USES. For the detection of glucose or other carbohydrates by *Molisch's* method. A 15% alcoholic solution is added to the solution to be tested. This is then floated on conc. sulphuric acid. A carmine red zone of contact shows the presence of glucose. Other carbohydrates and glacial acetic acid give similar reactions. $C_{10} H_{14} O = 149.7$.

TESTS. Thymol forms colorless, transparent monoclinic (or hexagonal) prisms, melting at 50°, boiling at 222° C. They have the odor of thyme. At 15° it dissolves in 333 parts of water; also in 0.5 parts of alcohol and easily in chloroform, ether, glacial acetic acid, etc. The commercial article is suitable for the reaction.

PREPARATION. From oil of thyme, monarda or ptychotis, which, besides thymol, $C_{10} H_{14} O$, contain thymene, $C_{10} H_{16}$, and cymol, $C_{10} H_{14}$. The fraction of the oil distilling above 200° C. is shaken with strong sodium hydrate solution, which dissolves the thymol and leaves the thymene, etc., to float on top. This is removed and from the solution in soda the thymol is precipitated by hydrochloric acid, and recrystallized from alcohol or from glacial acetic acid.

TIN AND ITS COMPOUNDS.

TIN, Sn.

USES. In blowpipe work tin is added to beads of borax or microcosmic salt for the purpose of reducing the metallic oxides therein dissolved. It is also used for the precipitation of selenium and arsenic from their solution in strong hydrochloric acid. If the acid is too dilute, it may be concentrated by addition of strong sulphuric acid. Tin is first dissolved, forming stannous chloride, and this precipitates the arsenic in brown flakes, containing a compound of tin and arsenic (*Bettendorf*). Sn 117.698,

TESTS. Pure tin has a silvery white lustre; crystals form in the quadratic system; spec. gr. 7.29; the metal is very ductile and may be reduced to thin foil. It melts at 228.5° C. and boils at white heat. Heated in air it oxidizes. It dissolves in hydrochloric acid, evolving hydrogen; in sulphuric acid, evolving sulphur dioxide; in cold, dilute nitric acid, without evolution of gas, forming stannous nitrate and ammonium nitrate; in conc. nitric acid it oxidizes to $Sn\ O_2$ without solution, evolving nitrous fumes. The gas escaping while tin dissolves in pure hydrochloric acid must not color paper moistened with silver nitrate, nor must the solution become colored by boiling with strong hydrochloric acid. This test of purity suffices for *Bettendorf's arsenic test.* For blowpipe use and for preparation of pure salts, the absence of other metals must be shown. The solution in dilute hydrochloric acid must yield with $H_2\ S$ a pure brown precipitate, from which ammonia water extracts nothing soluble, but which completely dissolves in warm yellow ammonium sulphide. The filtrate, after precipitation with $H_2\ S$, must yield neither color nor precipitate by treatment with ammonia and ammonium sulphide, nor, on evaporation, leave any permanent residue.

PREPARATION. Small amounts of pure tin may be made by fusing pure stannous chloride with potassium cyanide.

STANNIC CHLORIDE SOLUTION, $Sn\ Cl_4$, is used as an accessory in *Haswell's* process of titration of mercurous chloride by ferric chloride and potassium permanganate. To make it, stannic hydrate is first prepared from stannous chloride boiled with potassium chlorate and hydrochloric acid. The solution is precipitated by sodium hydrate, and the washed precipitated stannic hydrate is dissolved in hydrochloric acid. The solution must retain for three hours the red color communicated by a drop of permanganate. It is also used with pyrogallic acid to detect glycerin. See page 19.

STANNOUS CHLORIDE, $Sn\ Cl_2 + 2\ H_2\ O$.

USES. For the detection of gold by formation of purple of Cassius. For reducing mercuric chloride to mercurous and finally to metal. For a number of reductions depending on the formation of stannic salt by attraction of chlorine, e. g. platinic chloride into deep red colored platinous chloride. For detection of brucine by the deep purple-red color produced in the brucine solution after the red color has faded into yellow. For detection of arsenic by the brown compound of tin and arsenic formed in solutions in strong hydrochloric acid (*Bettendorf.*) For detection of arsenic as

yellow sulphide by the joint action of stannous chloride and sodium sulphite in hydrochloric acid solutions (*Schlickum*). See *Sodium Sulphite*, page 195. Also for the separation of caesium from potassium and rubidium, by removing it from a solution of their chlorides as a crystalline precipitate of *caesium-stannous chloride*, while potassium and rubidium remain in solution (*Stolba*). $Sn\,Cl_2 = 189.438$; $Sn\,Cl_2 + 2\,H_2O = 225.358$.

TESTS. Stannous chloride crystallizes with 2 mol. of water in transparent, colorless, monoclinic prisms. By cautious heating to 100° the water is lost; at 250° the anhydrous salt melts, and between 617° and 628° it boils and may be distilled without decomposition. It is easily soluble in water, but the solution rapidly absorbs oxygen and forms stannic chloride and oxychloride, unless kept in contact with metallic tin. When 1 part of the dry salt is boiled with 5 parts of pure conc. hydrochloric acid, the solution must remain clear and colorless. The dilute solution, acidulated with hydrochloric acid, must give no precipitate with barium chloride. Boiling the solution with excess of sodium hydrate must yield no ammonia. Other tests of purity are the same as directed for metallic tin.

PREPARATION. Pure tin in foil or granules is dissolved by heating with pure conc. hydrochloric acid, the tin being kept in excess. From the solution crystals may be obtained, or it may be diluted for use as test solution, so as to contain about 10% of the salt, metallic tin being kept in contact with it.

See also *Potassium Stannous Chloride* on page 171.

Stannous Sulphate, see *Potassium Stannous Sulphate*, page 171.

Toluidine, see *Para-Toluidine*, page 143.

TRI-ETHYL PHOSPHINE, $P\,(C_2\,H_5)_3$, is used to a very limited extent in the analysis of illuminating gas, to absorb $C\,S_2$, with which it forms a solid compound (Poleck). It is a liquid of spec. gr. 0.812, boiling at 127.5° C., and of peculiar, narcotic odor. It is made by heating phosphonium iodide, $P\,H_4\,I$, with three molecules of alcohol for many hours to 180° C. in s sealed tube. The resulting tri-ethyl phosphonium iodide, $P\,(C_2\,H_5)_3\,H\,I$, is decomposed by potassium hydrate into K I and triethylphosphine.

TRI-METHYL AMINE, $N\,(C\,H_3)_3$, has been proposed by *Vignon* to use instead of potassium hydrate to separate ferric hydrate, which is insoluble, from aluminium and chromium hydrates, which are soluble in it. The liquid is obtained as a bye-product of the manufacture of sugar from beets; it boils at 9.3° C., and is very soluble in water; it is characterized by a peculiar odor of herring pickle.

TRI-NITRO-PHENOL, $C_6H_3(NO_2)_3OH$.

(See *Picric Acid*, page 18.)

USES. Symmetric tri-nitro-phenol is usually called picric acid. In addition to the uses already enumerated (to precipitate albumen and alkaloids, and to detect glucose by the intense red color produced by the reduction, when heated with it in alkaline solution, of the picric to the picramic acid) it also serves to detect *creatinine*. A dilute aqueous solution of picric acid in dilute solution of sodium hydrate added to urine, or other solution of creatinine, produces quickly, *in the cold*, an intense red color, which, by excess of alkali, or by addition of acetic or hydrochloric acid, is changed to yellow. With *acetone* only a faint reddish-yellow color is given; with *creatine* a pure yellow, passing gradually into red; with *glucose* the deep red color is only produced by heating or by long standing in the cold (*Jaffe*).

Turmeric, see *Color Reagents and Indicators*, page 89.

URANIUM COMPOUNDS.

URANIUM ACETATE, $UrO_2(C_2H_3O_2)_2 + 2H_2O$.

(*Uranyl Acetate.*)

USES. Uranyl acetate precipitates phosphoric acid as acid uranyl phosphate, $UrO_2 . HPO_4 + 4H_2O$, which is insoluble in water and in acetic acid and forms a most eligible compound for gravimetric determination of phosphoric acid (*Knop*). It is also used volumetrically, according to *Pincus*, in empirical solution, made by standardizing with solution of sodium ammonium phosphate, so that 1 litre of the uranium solution corresponds to 5 gr. P_2O_5. The end of the reaction is indicated by "spotting" with potassium ferrocyanide, which gives a brown-red color with the least excess of uranium solution. In the same manner it is also used for titration of arsenic acid (*Boedeker*). It has been introduced into microchemical work by *Streng* for the detection of small amounts of sodium, based upon the formation of a double salt, $UrO_2(C_2H_3O_2)_2 . NaC_2H_3O_2$, which contains only 6.6% of Na and crystallizes in regular tetrahedra, easily distinguished from the rhombic or quadratic forms of the uranium acetate, which polarize light, while the tetrahedra do not. Addition of magnesium acetate forms a characteristic uranium-magnesium-sodium acetate, crystallizing in rhombic plates, which contains only 1.48% of Na. Uranium acetate is proposed by *Johanson* for

determination of the age of beer, as it gives increasing amounts of precipitate with increasing age up to a certain time. It is also used for precipitation of albumin (*Kowalewsky*). $Ur\,O_2\,(C_2\,H_3\,O_2) + 2\,H_2\,O = 424.058$.

TESTS. Uranium acetate crystallizes above 10° C. in yellow, rhombic prisms with 2 $H_2\,O$; below 10° C. it forms quadratic octohedra with 3 $H_2\,O$. Both forms are easily soluble in water and in alcohol. The acidulated solution must give neither color or precipitate with $H_2\,S$. With a mixture of ammonium carbonate and sulphide no precipitate must form, while the sulphide alone gives a brown precipitate. The filtrate from the latter must leave, on evaporation, no permanent residue. The commercial salt is sufficiently pure for volumetric work.

PREPARATION. Uranium pitch-blende, the most common uranium ore, containing $Ur_3\,O_8$, is powdered and dissolved in nitric acid. From the filtered solution yellow fluorescent crystalline needles of $Ur\,O_2\,(N\,O_3)_2 + 3\,H_2\,O$ are obtained. To remove foreign metals, if any, $H_2\,S$ is passed through the acidulated solution and the precipitate removed. The filtrate is then precipitated by ammonium hydrate and sulphide, the washed precipitate is digested with ammonium carbonate solution, which dissolves the uranium, leaving the other metals behind. The filrate is evaporated to dryness, heated with a slight excess of sulphuric acid and finally decomposed by barium acetate and the filtrate crystallized. The solutions are stable, if protected from light.

URANIUM NITRATE, $Ur\,O_2\,(N\,O_3)_2 + 6\,H_2\,O$.

USES. For the same purposes as the acetate. In titration of phosphoric acid the formation of free nitric acid, which would interfere, is prevented by addition of sodium acetate.

TESTS. From watery solutions uranium nitrate crystallizes with 6 $H_2\,O$ in greenish-yellow, rhombic prisms; from solutions containing much free nitric acid it crystallizes with 3 $H_2\,O$ in yellow, fluorescent needles. The tests for purity and preparation are the same as directed for the acetate. Addition of alcohol and exclusion of light make its solution quite stable.

UREA, $C\,O\,(N\,H_2)_2$.

Is occasionally used to detect furfurol by the violet color and peculiar absorption spectrum it produces with it on addition of a little hydrochloric acid (*Schiff.*) Also for the gasometric determination of nitrites. When excess of urea, a nitrite and dilute sulphuric acid are heated in a suitable apparatus, double as much nitrogen is liberated as the nitrate con-

tains: $2\,CO(NH_2)_2 + N_2O_3 = 2\,N_2 + CO_2 + (NH_4)_2CO_3$. By reversing the process and using an excess of the nitrite, the nitrogen serves as the measure of the urea decomposed (*Vivier*). $CO(NH_2)_2 = 59.976$.

A small quantity of urea may be prepared by saturating conc. ammonia water with carbon oxysulphide (prepared from potassium sulphocyanate and sulphuric acid). The solution is shaken with white lead, filtered, the rest of the lead removed by H_2S, and, on evaporating the filtrate, urea crystallizes in quadratic prisms.

VANILLIN, $C_8H_8O_3$, see on page 90, Color Reagents and Indicators, where the formula is erroneously given $C_8H_{10}O_3$, instead of $C_8H_8O_3$.

WATER, H_2O.

Uses. Pure water is employed as a general solvent and diluent; also for precipitation of substances insoluble in water from alcohol, acids and other solvents, e. g., cuprous chloride from hydrochloric acid, etc., and for decomposition of some metallic salts, e. g., bismuth nitrate into subnitrate, antimonic chloride into oxychloride, etc. Also for the formation of hydrates from anhydric oxides, calcium, barium, etc. $H_2O = 17.96$.

Tests. Pure water must be without color, taste or odor; must not change the color of testpapers; its freedom from solids in solution is shown by evaporating in a bright platinum capsule several Cc., which must not leave a trace of residue. Its freedom from such gases as can be expelled by heat must be insured by boiling immediately before use, that from others which may be absorbed from the atmosphere of the laboratory by its not giving precipitates with silver nitrate, potassium-mercuric iodide, barium hydrate, or color with starch, iodide of potassium and acid. After protracted standing in direct sunlight with silver nitrate it must not blacken it.

Preparation. From the purest obtainable natural water by distillation from any kind of still in which the condensing part consists of pure block tin, glass being objectionable on account of its yielding both alkali and silica to the condensing steam. The first and last fifths are to be rejected and only the middle three-fifths preserved in well-closed bottles of insoluble glass, safe from contact with absorbable gases or contamination by impure corks.

Wurster's papers, see pages 43 and 90.

XYLIDINE, $C_6H_3 . (CH_3)_2 . NH_2$.

Strips of paper dipped into a mixture of equal volumes of *ortho-xylidine* and glacial acetic acid and dried are used by *Schiff* as a most delicate reagent for furfurol, the least traces of which give to the paper a red color. As furfurol is among the products of dry distillation of carbohydrates, etc., the test may be extended to them. The commercial article is sufficiently pure.

YEAST is sometimes used for the detection and determination of glucose in urine by the fermentation test. A fresh wine or beer yeast should be selected and thoroughly washed before use. The amount of glucose may either be determined by measuring the CO_2 evolved in a fermentation tube or by ascertaining the loss of weight in a Fresenius & Will or a Geissler apparatus. The determination by difference of specific gravity, on account of the alcohol formed, is not very reliable.

ZINC AND ITS COMPOUNDS.

ZINC, Zn.

USES. Metallic zinc in the form of thin sheet, granules, dust or in the irregular, spongy form, cast so as to present much surface, is used to substitute for other metals in their salts and thus to precipitate them in the metallic state; or as a reducent either at high temperatures or by means of the nascent hydrogen produced when it is placed in contact with dilute acids or solution of caustic alkalies. Thus it serves to precipitate silver, mercury, lead, copper, antimony, tin, etc. It reduces in acid solutions ferric to ferrous salts, sulphurous acid to hydrosulphurous, H_2SO_2, and to H_2S, phosphorous acid to PH_3, etc. By the aid of acids or alkaline hydrates it serves to liberate H, SbH_3, AsH_3, H_2S, and thus serves especially for detection of arsenic and antimony. In alkaline solution, especially when in fine powder and aided by iron, it serves to convert nitrates to nitrites and to ammonia; in acid solution it is used to detect picric acid by producing a blue, di-nitro-cressol by a red color, etc. $Zn = 64.905$. (According to some recent investigators $Zn = 65.3$.)

TESTS. Pure zinc has a blueish lustre, crystalline fracture, and may be obtained in hexagonal pyramids (when containing copper in regular cubes). Spec. gr. $= 7$ to 7.2. It melts at 412° and boils at 940° C. It is easily soluble in dilute acids, also in potassium,

sodium and ammonium hydrate, in most cases evolving free hydrogen. The principal impurities are arsenic, cadmium, lead, iron and copper. Not all of them interfere with every reaction, so that the testing for purity need only be carried out in the special direction needed. Arsenic is detected by dissolving a piece of the zinc in pure, dilute sulphuric acid, of 8.3%, in a long test tube, covered with a cap of filter paper, moistened with a drop of saturated silver nitrate solution. If arsenic be present, a yellow compound, $Ag_3 As (Ag N O_3)_3$, will form (in case of traces only after some time). This slowly blackens, or, in contact with water, at once decomposes, leaving black metallic silver (*Gutzeit's arsenic test*). Immediate blackening indicates presence of antimony, sulphur or phosphorus. The solution in the test tube should be free from black flocculi of undissolved lead. The filtrate, acidulated, if not already acid, should give no precipitate by passing $H_2 S$ to saturation; after filtering and neutralizing by ammonia, ammonium sulphide should give a pure white precipitate, and the filtrate from this should leave no residue on evaporation and ignition on platinum foil. A drop or two of deci-normal permanganate solution added to the solution of zinc in sulphuric acid must give it a permanent red color, if no iron is present.

PREPARATION. Very few specimens of commercial zinc are strictly pure, and even some sold as strictly pure will not stand Gutzeit's arsenic test, and can not be used in forensic analysis; some analytical operations, however, permit the use of zinc of less purity, and require only absence of certain impurities to which testing and purification must be specially directed.

To obtain *zinc free from arsenic*, various processes may be chosen.

Selmi directs to stir ammonium chloride into the fusing metal, which removes the arsenic as volatile $As\ Cl_3$.

L'Hote uses 1 to 1.5% of magnesium chloride, which from the melted zinc removes arsenic and antimony, but leaves Mg.

Stolba forms at the end of a wooden rod little balls of sulphur and plaster of paris; when the melted metal is stirred with the ball, sulphur and water vapor are evolved and agitate the fused mass. When no more vapors escape the ball is withdrawn and the scum scraped off, and the remaining metal is now freed from arsenic, iron and lead. If necessary, the process is repeated.

To obtain zinc absolutely pure, it must be carefully distilled from a clay retort, changing the receiver after the first portion, containing the arsenic and cadmium, has passed over. The distillation is interrupted before the whole of the metal has passed

Lead and iron remain in the retort. If the product is not absolutely pure, it must be redistilled.

Zinc amalgam, made by heating 1 part of zinc with 3 parts of mercury, is sometimes used to convert potassium iodate into iodide, so as to be used in starch solution for showing presence of chlorine, etc. (*Morse and Burton*).

ZINC CHLORIDE, $Zn\ Cl_2$.

USES. A boiling saturated aqueous solution of zinc chloride rapidly dissolves silk, while it does not affect wool or cotton; hence, it is employed for examination of textile fabrics (*Remont*). A solution of 1 part in 30 of water is used as reagent for glucosides, alkaloids, etc., by evaporating the specimens with it to dryness. Strychnine and veratrine give red color; narceine, olive green; thebaine, berberine and quinine, yellow; salicin becomes red-violet; santonin, blue-violet; cubebin, crimson; digitalin, chestnut-brown (*Czumpelitz*). Added to the glucose solution towards the end of Fehling's titration, it promotes the separation of Cu_2O, and thus facilitates the observation of the end point (*Beckmann*). A solution of 50 parts of zinc chloride and 16 parts of potassium iodide, dissolved in 17 parts of water, and then saturated with iodine, converts cellulose into starch and reveals its presence by the deep blue color; hence, it is especially useful in microscopical work on vegetable structures. (*Schulze*.) With creatinine it forms a compound easily recognized under the microscope by the peculiar rosette shape of its crystals. A saturated solution of $Zn\ Cl_2$ in water boils at 300° C., and is used occasionally as a bath for maintaining that temperature. $Zn\ Cl_2 = 136.645$.

TESTS. Anhydrous zinc chloride forms a white deliquescent mass, boiling between 676° and 683°, and may be distilled without decomposition. In water and in alcohol it readily dissolves. From aqueous solution acidulated with $H\ Cl$ octohedral crystals of $Zn\ Cl_2 + H_2O$ may be obtained, but without surplus of acid the solution cannot be evaporated without decomposition and formation of oxychloride, which, however, rarely interferes in the reactions. The tests for purity are the same as directed for the metal.

PREPARATION. Anhydrous zinc chloride (which is rarely needed) may be made by heating zinc in chlorine gas, or by distilling the commercial salt, which yields $Zn\ Cl_2$, leaving $Zn\ O$ as a residue. For most purposes a solution is required, which is made by saturating pure hydrochloric acid with pure zinc.

ZINC IODIDE, $Zn\,I_2$.

USES. Zinc iodide added to starch solution serves for detection and as indicator in the titration of chlorine, bromine, nitrous acid, etc., which render the starch blue through liberation of iodine. With hydrogen dioxide it produces the same result (*Schoenbein*); in acid solutions a little cupric sulphate and ferrous sulphate must be added to render the reaction sensitive (*Traube*). With potassium iodide zinc iodide forms a double salt, which is used to precipitate alkaloids and serves especially for detection of narceine, whose precipitate gradually forms hair-like crystals, which after 24 hours' standing assume a blue color (*Dragendorff*). $Zn\,I_2 = 318{,}019$.

TESTS. Zinc iodide crystallizes from watery solution in deliquescent regular octahedra. It melts at 446° C., and at higher temperature sublimes without decomposition, forming needle-shaped crystals. For the purposes above stated the salt is sufficiently pure if when dissolved in starch solution it gives no color, even when dilute sulphuric acid is added.

PREPARATION. 64.905 parts of finely powdered zinc are rubbed in a mortar with 126.557 parts of iodine until the color has disappeared, and then either sublimed or dissolved in water and the crystals well dried and preserved.

The *starch solution containing zinc iodide*, used for detection of nitrites in drinking water, etc., is made by dissolviug 4 gr. of starch in a boiling solution of 20 gr. zinc chloride in 100 Cc. of water, adding 2 gr. of zinc iodide, filling up to a litre and filtering. The solution should be placed into small vials and kept in the dark.

ZINC SULPHATE, $Zn\,S\,O_4 + 7\,H_2\,O$.

USES. In the analysis of gaswater, zinc sulphate serves to precipitate the sulphocarbonates; the precipitate, after washing with cold water, is brought into a flask containing water connected with a receiver containing tri-ethyl-phosphine. When heated to boiling the zinc sulphocarbonate decomposes and the vapor of $C\,S_2$ is absorbed by the tri-ethyl-phosphine. $Zn\,S\,O_4 + 7\,H_2\,O = 286.449$.

TESTS. Zinc sulphate crystallizes in colorless, rhombic prisms, soluble at 15° in 0.67 parts, at 100° in 0.167 parts of water. It is tested for impurities in the same manner as the metal, but for the above use the commercial article, free from iron, is sufficiently pure.

PREPARATION. Pure zinc is dissolved in dilute sulphuric acid and crystallized.

ZINC SULPHHYDRATE, $Zn(SH)_2$.

USES. To prepare pure hydrogen sulphide, free from arsenic, *Hager* proposes to use zinc sulphhydrate, $Zn(SH)_2$, formed into pencils. It is also used to detect free mineral acids in vinegar by the liberation of H_2S; pure acetic acid does not decompose it (*Foehringer*). $Zn(SH)_2 = 130.873$.

PREPARATION. Pure zinc sulphate is either precipitated by ammonium sulphide and the white precipitate washed and dried, or the sulphate is boiled with pure sulphur and potassium hydrate, and the washed precipitate moulded into pencils with 10% of white bolus (*Hager*).

ADDENDA.

BENZOYL CHLORIDE, $C_6H_5 . COCl$.

USES. For detection of alcohol, which is converted by it into ethyl benzoate, $C_6H_5 . COO . C_2H_5$, an ester of peculiar pleasant odor, even when only a small quantity is present in water. The ester dissolves in the surplus of benzoyl chloride, whose disagreeable penetrating odor disguises that of the ethyl benzoate. Addition of potassium hydrate solution decomposes the surplus of benzoyl chloride, while ethyl benzoate remains unaffected, and may now be recognized by its odor. A few Cc. of liquid containing 0.1% of alcohol give a decided reaction (*Berthelot*).

Benzoyl chloride has also been recommended by *Baumann* (and his collaborators, *Goldmann*, *Wedenski* and *Udransky*) to detect cystine in urine, etc., by converting it in alkaline solution into the insoluble sodium compound of benzoyl-cystine, in which the cystine is recognized by its sulphur reaction, etc. Also for precipitating glucose from urine made alkaline by sodium hydrate, as a benzoyl compound in which the glucose may be identified by the red color reaction it gives with alpha-naphthol and conc. sulphuric acid. $C_6H_5 . COCl = 140.148$.

TESTS. Benzoyl chloride is a highly refractive liquid of penetrating disagreeable odor, spec. grav. 1.25 at 15° C. By aid of a freezing mixture it is obtained in transparent crystals, which melt at —1° C. and boil at 198.3° C. It easily dissolves in ether and carbon disulphide. Water decomposes it, slowly at ordinary temperature, rapidly when hot, into benzoic and hydrochloric acid. It is sufficiently pure when it forms ethyl benzoate with alcohol, recognized by its pleasant odor after the surplus of benzoyl chloride has been decomposed by potassium hydrate.

precipitated by cinchonine (or other alkaloids). It also serves for volumetric determination of querco-tannic acid, according to *Wagner's* method, by means of a solution containing 4.523 gr. of cinchonine sulphate in 1 litre, corresponding to 10 gr. of querco-tannic acid. The method is not very accurate. The nitrate is used with potassium iodide to detect bismuth, in nitric acid solution, by an orange precipitate (*Leger*). 1 gr. cinchonine, dissolved in dilute nitric acid, is added to a solution of 2 gr. potassium iodide and water enough to make 100 Cc. The pharmacopœial preparation is of sufficient purity. $C_{19} H_{22} N_2 O = 293.408$.

Ethylic ether, page 102; when a specimen is shaken in a test tube with a drop of mercury the metal should remain perfectly bright; a tarnish indicates the presence of sulphur *(L. L. de Koninck)*.

Alpha-NAPHTHYL-AMINE, $C_{10} H_7 N H_2$.

USES. For the detection of nitrous acid, which, with the solution of *alpha*-naphthyl-amine in glacial acetic acid, produces a yellow color, turning violet-red on addition of hydrochloric acid. Also for detection of hydrogen dioxide and other active oxidizers, which convert *α*naphthyl-amine, in aqueous solution, into violet-blue *oxy-naphthylamine* or *naphthameine* (*Wurster*).

In conjunction with sulphanilic acid, it serves as Griess' reagent to detect small quantities of nitrites, see page 20. Hydrogen dioxide, which, especially in presence of sodium chloride, converts ammonia into nitrites, may thus be detected by Griess' reagent in minute quantities, as in saliva. If urea, leucine, tyrosine or similar amido-derivatives are present, together with the nitrite, the sulphanilic acid of Griess' reagent is decomposed by them and the violet-blue color of naphthameine appears, the same as if the *α*naphthyl-amine were used alone (*Wurster*). $C_{10} H_7 N H_2 = 132.761$.

TESTS. Commercial *alpha*-naphthyl-amine, after recrystallization from alcohol, is sufficiently pure for the reactions above described. It is prepared in large quantities by the reduction of nitro-naphthalin for the manufacture of magdala-red and other diazo-colors. It forms white crystalline masses, sometimes with a gray or brownish tint. It has a penetrating, unpleasant odor which distinguishes it from the inodorous *beta*-naphthyl-amine. It melts at 50° and boils at 300° C. It is quite soluble in alcohol, ether, glacial acetic acid or aniline, but requires 600 parts of cold water for solution. As the solution deteriorates by keeping, it should only be made in small quantities shortly before using, and, if preserved at all, should, be kept dark and closely guarded

against accidental absorption of nitrous fumes. The solutions for *Griess' test* for nitrites are made as follows: 0.1 gramme of *sulphanilic acid* (see page 20) is dissolved in 30 Cc. of dilute acetic acid; 0.1 gr. *a*naphthyl-amine is boiled with 20 Cc. distilled water, decanted from the blueish residue, and added to 180 Cc. of dilute acetic acid. The liquid to be examined is then mixed with half its volume of the sulphanilic solution, heated to 80° C. and the naphthyl-amine gradually added until the color, at first yellow, turns red *(Ilosvay)*. If very carefully preserved, the solutions may be mixed and added to the specimen.

USE OF THE SPECTROSCOPE.

When white light passes through a prism whose planes meet at an acute angle, the rays composing it are dispersed into a color-spectrum, in which the violet rays are refracted farthest from their original direction, the red rays least. If a screen with a narrow slit is interposed between the source of light and the prism, the colorbands of the spectrum are yet continuous if the light emitted contains all the rays composing white light. But if the source of light emits only rays of one color, then the image of the slit appears as a bright line of that color. If rays of several colors are emitted from the source of light, we have a discontinuous or interrupted spectrum consisting of images of the slit in the several colors with dark spaces between, and giving the appearance of bright colored lines upon a dark background. Light emitted by solids at white heat produces a continuous spectrum. A platinum wire held in the flame until it becomes incandescent, or the bright flame of the gas-lamp or candle containing incandescent carbon, give white light and a continuous spectrum. Gases or vapors, when sufficiently heated to become luminous, emit, under ordinary pressure, color rays which are dispersed into an interrupted spectrum of bright lines; with increasing pressure and density these lines spread into diffuse luminous bands, and finally form a continuous spectrum. A few solids, erbium, didymium and thulium, give, when heated, a continuous spectrum of moderate brightness as a background upon which certain brilliant lines are seen as an interrupted spectrum. When light of high intensity passes through transparent media, a portion of it is absorbed. When this occurs uniformly for all rays, the spectrum merely loses some of its brilliancy. But when particular rays are absorbed more than others, certain parts will be wanting in the continuous spectrum, and are represented by dark lines or bands.

PREPARATION. Four parts of benzoic acid are distilled with 7 parts of phosphorus pentachloride, the distillate is received in a flask surrounded by a freezing mixture, and the crystals, after draining, are purified by redistillation, preserving the fraction distilling near 198°to C.

CADMIUM CHLORIDE, $Cd\ Cl_2 + 2\ H_2\ O$.

USES. Cadmium chloride very rapidly and completely precipitates from even very dilute solutions of hydrogen sulphide or alkaline sulphides, all of the sulphur as yellow cadmium sulphide, but is not affected by hyposulphites (thiosulphates). Hence, it is used in the analysis of mineral waters to precipitate together all the sulphur present as alkaline sulphide or free hydrogen sulphide. The precipitate very frequently carries down with it some undecomposed cadmium chloride.

TESTS. Cadmium chloride forms colorless prisms of the formula $Cd\ Cl_2 + 2\ H_2\ O$, which easily lose water in dry air or by heating. At 20° C. 100 parts of water dissolve 140.8 of $Cd\ Cl_2$. The anhydrous salt melts at 541° C. and at higher temperature sublimes unchanged, forming colorless, shining scales. The solution, slightly acidulated by H Cl, should yield with $H_2\ S$ a precipitate of pure yellow color. The filtrate from this should, on evaporation, leave no permanent residue. The yellow precipitate should yield nothing to ammonia water (absence of arsenic).

PREPARATION. Pure metallic cadmium is dissolved in somewhat diluted hydrochloric acid. The solution is hastened by contact with metallic platinum (wire or foil). The concentrated solution is crystallized and, if great purity is desired, is sublimed.

CARBAZOL $(C_6\ H_4)_2\ N\ H$.

USES. A solution of carbazol in conc. sulphuric acid, of spec. gr. 1.84, assumes a green color in contact with nitrates, nitrites, chromates, ferric salts, chlorine, bromine, iodine and other oxidizing agents. So intense is this green color, that even 0.0027 mgr. of nitric acid render it distinctly visible. Hence, it is recommended for detection of nitrates in drinking water, and their rapid colorimetric determination by comparison with the color produced in standard solutions of pctassium nitrate. The water, if necessary, is freed from iron by alkaline hydrate and from chlorides by silver sulphate, and 2 Cc. are mixed with 4 Cc. of conc. sulphuric acid and cooled. To this 1 Cc. of the solution of carbazol is added, and after thorough mixing the color is compared with that of the standard (*Hooker*).

Tests. Carbazol or diphenylimide crystallizes in shining white scales, which melt at 238° C. and sublime unchanged at 352° C. It is insoluble in water, slightly soluble in cold, more in hot alcohol, ether, chloroform, carbon disulphide, benzol and glacial acetic acid, and quite readily in conc. sulphuric acid. The latter solution, at first brownish-yellow, turns olive green after some hours, while that in acetic acid remains unchanged for a considerable time. The crude article, obtained as a bye-product of the manufacture of aniline and of anthracene, is sufficiently pure if its solution turns intensely green with a trace of nitric acid.

Preparation. During the manufacture of anthracene the fraction distilling between 320° and 360° C. is preserved separately, and from it the carbazol contained in it is extracted by acetic ether. From the dry extract pure carbazol may be obtained by dissolving in toluol and adding picric acid. The carbazol picrate separates in red prismatic crystals. These are treated with ammonia water, when carbazol remains insoluble, while ammonium picrate dissolves. The product is purified by recrystallizing from hot absolute alcohol.

CARBON DIOXIDE, CO_2.

Uses. To displace the air in apparatus during the distillation of easily oxidized substances, or when the presence of either oxygen or nitrogen would be objectionable, as in elementary organic analysis, for nitrogen determination, according to *Dumas*, where carbon dioxide is introduced, either into the open combustion tube from without or generated within the closed tube. Water saturated with carbon dioxide occasionally serves in the analysis of soils, to extract those carbonates insoluble in pure water, which by conversion into dicarbonates become soluble, the apparatus used permitting saturation under higher than ordinary atmospheric pressure. Also to extract bloodstains from cloth (*Struve*).

The gas used for these purposes is either liberated by heat from sodium dicarbonate, which yields CO_2 and H_2O, or, if the presence of moisture is to be avoided, from anhydrous neutral sodium carbonate and potassium dichromate, or from manganous carbonate, etc. Or it is evolved from calcium or other carbonates by addition of hydrochloric acid. In such case it must be purified by passing through wash bottle and drying apparatus. Pure materials should be used to avoid introduction of volatile impurities.

CINCHONINE, $C_{19}H_{22}N_2O$.

Uses. Solution of the sulphate is used to distinguish tannic acid, whose solution is precipitated, from gallic acid, which is not

for placing the tubes, holding the colored liquids between the slit and the source of light. A bright flame may be substituted for reflected sunlight, but has the disadvantage that it shows no Fraunhofer lines, and these valuable guides to the position of the absorption bands must be dispensed with. The tubes for holding the solutions may be either ordinary test tubes, of 1 Cm. diameter, or glass cells with flat parallel sides, or of wedge shape, so as to allow the examination of different thicknesses of the liquid.

To observe the *emission spectra* of colored flames, the instrument, after focussing, is directed (with the slit perpendicular) toward the centre of the upper part of a narrow, non-luminous Bunsen flame, into the lower part of which the substance is introduced, supported on a platinum wire. Use of a broad flame, or directing toward the edge, or an oblique position of the slit, will give rise to secondary images, which greatly interfere with the accuracy of the result. The platinum wire is supported on a stand, and by adjustment in height and rotation can be easily brought and steadily maintained in any part of the flame most suitable for the volatilization of the substance. The wire, about 0.5 to 0.6 Mm. thick, is bent into a loop of a width differing with the fusibility of the substance, and must be thoroughly cleansed before each observation by first soaking in water or dilute acid, rinsing in distilled water and then heating in the hottest part of the flame until it no longer produces either color or even the faintest spectrum. It is then charged with the substance to be examined, either by immersing the redhot wire-loop into its powder, or by fusing a bead to it in the flame, or by means of the blowpipe. In some cases it may be dipped into the solution. The spectrum must be observed accurately at the first insertion of the substance into the flame, as some substances are very volatile or are rapidly decomposed, and then fail to give the characteristic spectrum of their volatile salts (e. g. $Ca\,Cl_2$). The observation must then continue for some time, to give opportunity for the more volatile substances, whose brilliant spectrum obscures the fainter lines, to evaporate. The observer must make himself familiar with the spectrum of the Bunsen flame (see plate, VIII, 21 C O), so as not to confound its lines (which in instruments of small dispersion coalesce into broad but faint lines) with similarly situated lines, especially those of boracic acid (see plate, IX, 14, $B_2\,O_3$).

EMISSION SPECTRA of the following metals and of some of their salts may be produced at the temperature of the Bunsen flame :

Lithium, sodium, potassium, rubidium, cæsium, calcium, strontium, barium, magnesium (metal only), thallium, indium, gallium, lead, copper, cadmium, gold, tin and manganese.

The lesser volatility of the more refractory metals forbids their recognition by flame spectra, and the electric spark or Geissler tubes must be resorted to, or fusible glasses, colored by their salts, may be prepared in films and their absorption spectra observed, e. g. cobalt, erbium, didymium.

Too great a volatility also interferes by evaporating the substance before it attains the temperature of luminosity, and thus most metalloids give no flame emission spectra. Those of carbon ($C\,O$, plate, VIII, 2), and boron ($B_2\,O_3$, plate, IX, 14), are most easily obtained, while those of sulphur, selenium, tellurium, phosphorus, arsenic, chlorine, iodine, etc., are obtained, only with great difficulty, by burning the vapor mixed with hydrogen, or by rendering it luminous in Geissler tubes.

The lines composing the spectrum of an element are designated in order of their prominence and brilliancy by the chemical symbol of the element followed by letters of the Greek alphabet. The following are the spectra of most importance to the analyst:

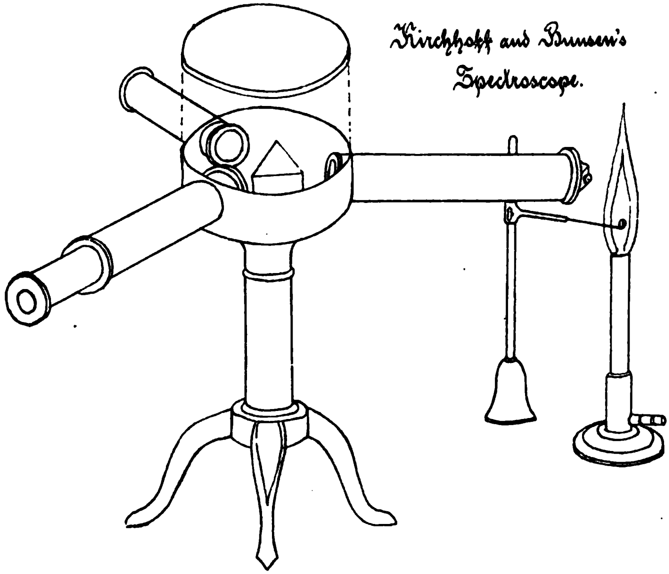
LITHIUM (VIII, 3) at lower flame temperatures shows a single brilliant red line, Li *a*, at 670.6. At higher temperatures Li *b* appears at 610.2, nearer to the sodium line D and much fainter. The blue line at 460.4 is only produced by the high temperature of the electric arc.

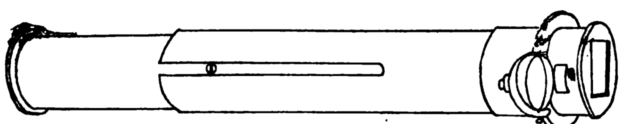
SODIUM (VIII, 4) shows, with low dispersion, a single yellow line at 589.5, corresponing to D in the solar spectrum. This is subdivided into two lines by higher dispersion, and these again are resolved into groups by the best instruments. The line is so intensely bright that even the smallest traces of sodium (dust floating in the air, etc.) produce it, and it is difficult to obtain a spectrum in which the line does not flash up occasionally. This, however, is sometimes of use for estimating the position of other lines.

POTASSIUM (VIII, 5) ordinarily shows but a single line in the red, K *a*, at 769.8, near A. With better instruments, a faint line is visible at 766.2. At higher temperature (burning of $K\ N\ O_3$ or $K\ Cl\ O_3$) K *b* is seen as a sharp line in the violet end at 404.4, which at lower temperature appears as a faint halo only. The luminosity in the centre of the spectrum is by higher power resolved into many lines.

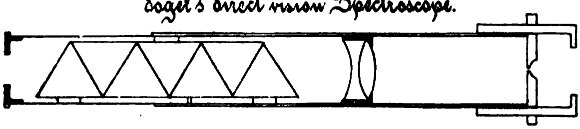
RUBIDIUM (VIII, 6) shows, with feeble dispersion, 2 lines, one red, the other deep blue; with more powerful instruments both of these

Kirchhoff and Bunsen's Spectroscope.

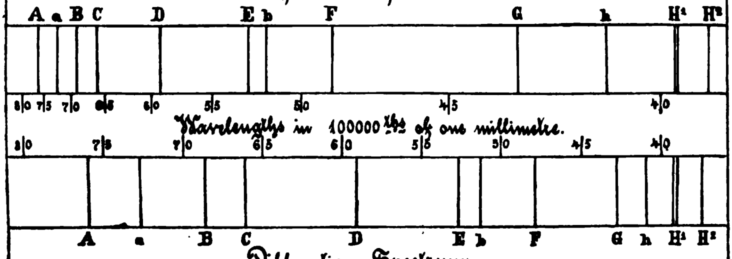




Vogel's direct vision Spectroscope.



Refraction Spectrum.



Diffraction Spectrum.

Of such origin are the dark lines in the solar spectrum, mapped by Fraunhofer in 1814, and since bearing his name. As a general rule, transparent media absorb those rays which they would emit when highly heated and colored substances absorb the rays of their complementary colors. Instruments for the observation of spectra, called spectroscopes, are of various construction, some very complicated and of powerful dispersion, for the use of astronomers, some very simple.

In the following pages a concise description will be given of such phenomena only as may be observed by means of the simple spectral apparatus usually kept in analytical laboratories. The emission spectra of such metals and salts, as are capable of being produced at the temperature of the Bunsen gas burner, are valuable means of their identification. Absorption spectra of solutions are also very useful for the recognition of coloring materials, etc. From the great number of the latter already described in works dealing especially with this topic, a few only have been selected, which are interesting, either on account of serving as color indicators, or forming the result of specific reactions, or being the means of identifying blood stains or poisoning by inhalation of deleterious gases, or *vice versa*, recognizing the gas by the changes produced by it in the coloring matter of blood.

Of the various instruments employed in the laboratory, the form adopted by Kirchoff and Bunsen is represented on plate VII, as constructed in the simplest manner by Desaga and others. A flint glass prism, contained in a dark box, receives light through the adjustable slit at the end of one of the tubes, the spectrum is observed through a small telescope. For measuring the position of the colored images of the slit which form the lines of the spectrum, a photographed scale is inserted into the end of a third tube, and reflected so as to coincide with the color spectrum observed by the telescope. A small prism, covering half the length of the slit, is often added, to introduce spectra of known substances, exactly superimposed over those of the substance under examination, so as to recognize coincidences and differences by comparison.

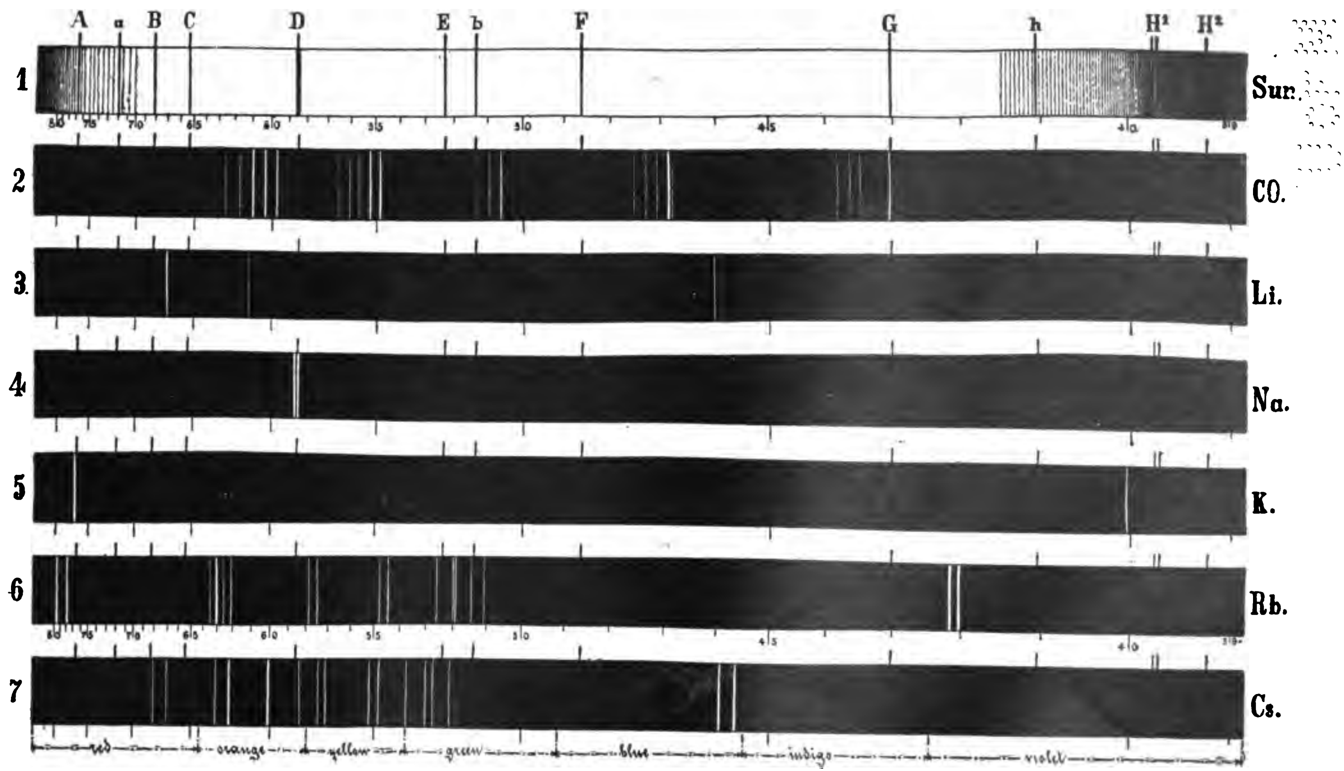
In more elaborate instruments the telescope turns upon a pivot, and the position of the lines is determined by measuring their angular difference upon a graduated arc provided with nonius. Another form of instrument, the *direct vision spectroscope*, contains, in a straight tube, a number of small prisms (from 3 to 7), arranged to refract the rays of light so as to leave the instrument nearly in the same direction in which they entered. The plate represents the instrument devised by Prof. Vogel, which, in

addition to the slit and the prisms, has a collimator lens, and a mirror to reflect light from a second flame upon the comparison prism. No arrangement, for measuring the position of lines, is attached to this instrument; in observing flame spectra, the comparison prism answers as a substitute, while for absorption spectra, observed with reflected solar light, the position of the Fraunhofer lines, seen at the same time, serves as a guide.

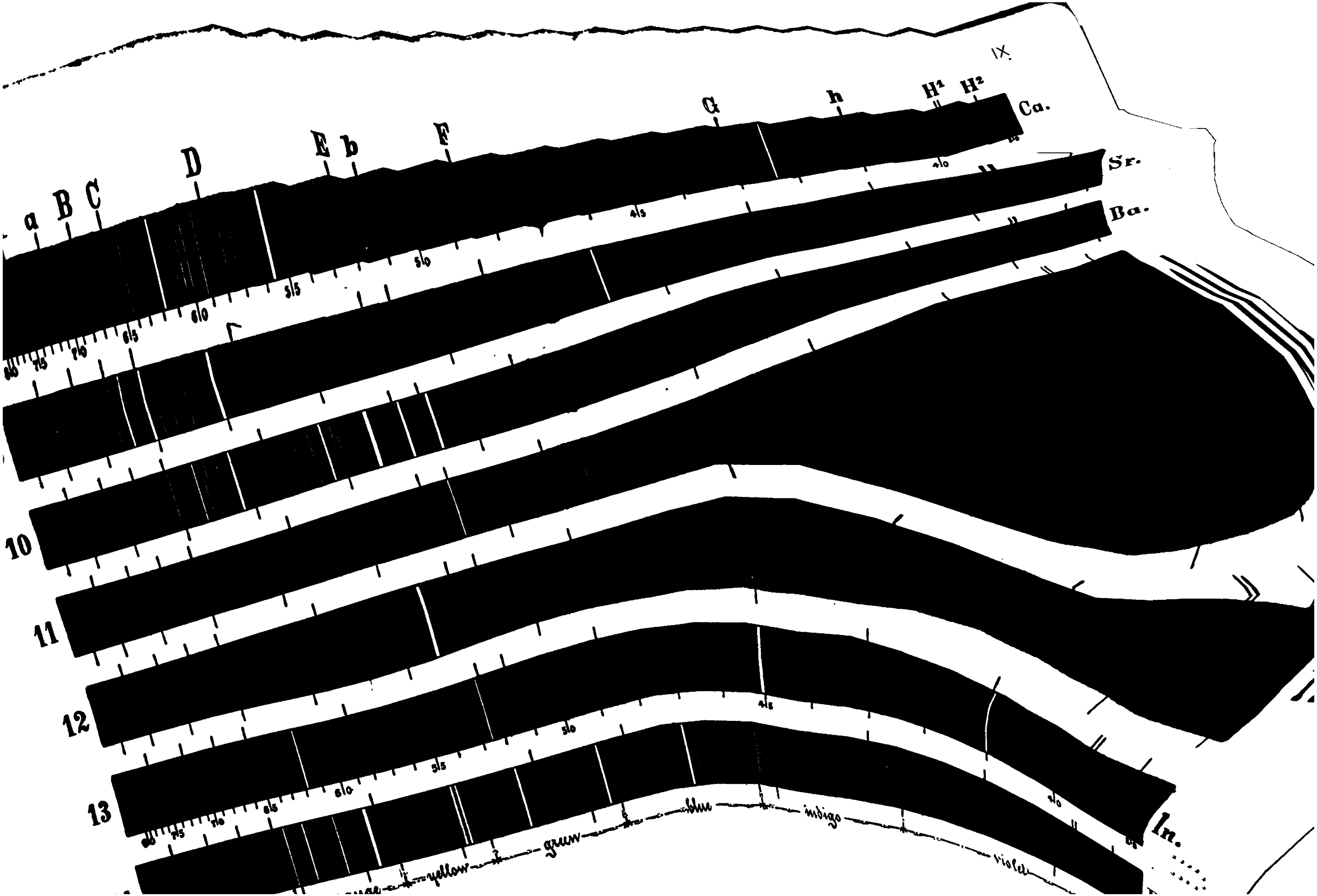
For accurately recording the position of lines and bands, it is best to give the wave length (λ) of the ray, which is generally done in millionths of a millimetre. For ordinary purposes, diagrams with a scale attached suffice, but it must be remembered that all spectra produced by *refraction*, not only differ according to the density of the glass or other material of the prism, but also condense the red end of the spectrum out of all proportion with the violet end. This will best be seen by comparison with the *diffraction* spectrum, produced by a fine grating, in which the lines, differing by an equal measure of their wave-lengths, appear at equal distances from each other, while equal differences in wave-length are distorted to very unequal measures in the spectrum produced by refraction by prisms (see plate). In the plates illustrating this chapter, the refraction spectra are represented as seen with the instruments in common use. The scale, immediately below the spectrum, indicates the wave-length (λ), the figures from 40 to 80, representing one hundred thousandths of millimetres, as there is not room to give the third figure (400 to 800) necessary for the usual expression of wave-lengths in millionths of one millimetre.

When an observation is to be made, the instrument is first directed towards the clear sky, or a white wall, and the opening of the slit and adjustment of the focus of the eyepiece so arranged as to give the sharpest possible definition of the fine dark lines running parallel to the colorbands. Of these lines, the most prominent ones were designated by Fraunhofer by letters of the alphabet, beginning at the red end of the spectrum. When the instrument is directed to the sun's disk, a very brilliant spectrum appears extending from near the line A, in the red, to beyond the line H in the violet end of the spectrum. Such a sight, however, must be taken with extreme caution, and for seconds only, as it might injure the eye. It is best to use the reflected light of a bright sky or a white wall, when a portion of each end of the colorspectrum will become shaded (see plate VIII, 1, sun. The position of the colorbands is indicated at the bottom of each plate). The instrument is then secured in this position, if absorption spectra are to be observed, and a suitable holder arranged

VIII



A
a
B
C
D
E
b
F
G
h
H¹
H²
1
2
3
4
5
6
7
Sur.
CO.
Li.
Na.
K.
Rb.
Cs.
red
orange
yellow
green
blue
indigo
violet


IX.
a B C D E b F G h H¹ H²
Ca.
Sr.
Ba.
10
11
12
13
In.
80 75 70 65 60 55 50 45 40
yellow
green
blue
indigo
violet

BORON TRIOXIDE (IX, 14) and boracic acid, $H_3 B O_3$, color the outer envelope of the flame green and produce a spectrum composed of diffuse bands at 580.7, 548.5, 543.9, 519.2, 494.1 and 472.1; also lines at 639.7, 621.0, 604.1 and 452.9.

The emission spectra of *erbium*, *didymium* and *thulium* are seen, when the oxides or salts are heated to incandescence, as bright lines upon a background of a continuous spectrum.

ABSORPTION SPECTRA of some metals may be observed by fusing them with borax, microcosmic salt or alkaline silicates and forming a thin film of the fused mass between the sides of the platinum wire loop. With some it suffices to interpose a solution between the source of light and the instrument. Some give the absorption lines or bands when the light reflected by them is examined in the spectroscope.

ERBIUM CHLORIDE (XII, 33) shows 3 absorption lines, having wavelengths of 653.4, 523.1 and 487.4. Its emission spectrum is similar.

DIDYMIUM CHLORIDE (XII, 34) shows 8 lines at 730.7, 578.8, 574.7, 571.9, 521.9, 520.5, 482.2 and 469.1, either bright, when heated, or as absorption lines.

THULIUM OXIDE, when heated, shows upon a continuous spectrum as background a bright red line at 684.0 and a blue one at 476.0. Its salts show two absorption bands at 684.0 and at 465.0.

POTASSIUM PERMANGANATE (XII, 32) in aqueous solution shows a remarkable absorption reaching from 589.0 to 482.0, in which 5 distinct bands are shown at certain dilutions (0.01%), of which the second one, counting from the red end, is the strongest. With greater concentration of the solution the 3 middle ones coalesce; in greater dilution all gradually fade, and at last only the second band remains visible.

COBALT SULPHOCYANATE (XII, 35) yields with ether a violet-blue solution whose absorption spectrum, visible even in great dilution, is very characteristic. The violet end is shaded to G, then a narrow absorption band occurs at 560, and a very broad and dark one from 602.0 to 660.0; from thence a dimly lighted interval reaches to 700.0, and the rest of the red end is dark.

When organic liquids showing absorption spectra of one or more bands are to be examined, it is almost indispensable to use the accessory prism for bringing the spectrum of a substance of known purity into contact with the one to be investigated. The appearance of the two superimposed spectra then resembles those on the

plates Nos. 18, 20 and 21, and admits of close comparison and the accurate observation of coincidences or differences. With the same coloring material a change of the solvent often produces very marked and decided differences, and the degree of saturation or dilution gives rise to various appearances.

For the observation of these absorptions, an instrument of moderate dispersion is preferable to one of high power, and the ordinary pocket spectroscope is quite sufficient for such work if provided with a prism for comparison. Great help is also derived from a wavelength scale engraved on a glass disk and inserted into the focus of the ocular. When minimal amounts of blood or other coloring matters are to be examined, the spectroscope is sometimes used in combination with the microscope by inserting it into the place of the ocular.

Considerable difficulty is sometimes experienced when substances produce mixed spectra. Thus blood partially saturated with carbon monoxide gives the mixed spectra of oxyhaemoglobin (XI, 23) and C O haemoglobin (XI, 25), and is difficult to distinguish from the spectrum of pure reduced haemoglobin (XI, 24). In such cases the superimposing of spectra of known substances for comparison and the addition of reagents to the liquid will often decide the question, for a number of spectra are changed in position by the addition of a drop of acid or alkali, by shaking with air, etc.

BRAZILIN (X, 15), see page 58, in aqueous solution shows a dark band from E toward D, the nucleus extending from 527 to 557, with gradual shading off at both ends. The red end of the spectrum is absorbed from a, the violet end from half way between b and F increasing gradually towards the more refrangible end. It may be readily mistaken for oxyhaemoglobin in sufficient concentration to let its central bands coalesce (XI, 22). Addition of a little acid clears up the absorption band of brazilin, while alkalies increase its intensity.

COCHINEAL (X, 16, 17), see page 77, contains the glucoside *carminic acid*, which by the action of alum may be split up into *carmine red* and glucose. Both give similar spectra. *Carminic acid* absorbs the violet end completely to 450.0, G, and then shades off gradually to 460.0 between E and D ; two dark bands occur with slight shading between. Addition of alkali completely clears up the intervening space and moves the bands somewhat towards the red end. Carmine red absorbs the violet, beginning at 412.0 and gradually darkening toward the end. The two central bands are quite separate; the one nearest to the violet end is broader and

are resolved into double lines, while the faint luminosity in the orange, yellow and green is resolved, at high temperature, into lines as shown in the plate. The blue lines are : Rb *a* at 421.6 and Rb *b* at 420.2 ; the red lines : Rb *c* at 780.0 and Rb *d* at 795.1.

CAESIUM (VIII, 7) gives a spectrum similar to rubidium, but the brilliant lines are brighter blue and the fainter line orange instead of red. Cs *a* at 456.0 ; Cs *b* at 459.7 ; Cs *c* at 621.9. The other lines at lower temperature coalesce into a luminous halo, but appear, at higher temperature, as distinct lines. The volatility of caesium causes a rapid disappearance of its spectrum.

CALCIUM (IX,8) shows two very prominent lines : an orange one, Ca *a* 620.6 ; a green one, Ca *b* at 555.3 ; a somewhat fainter violet blue, Ca *c* at 428.6, nearly coincident with the rubidium line, and a number of finer ones in red, orange and yellow. The orange and green lines persevere longest, though fainter after the decomposition of the volatile chloride, and become more brilliant again on moistening the platinum wire with hydrochloric acid.

STRONTIUM (IX,9) shows seven lines in the red and orange and one fine blue. The wavelengths of the brightest are Sr *a* 603.1 ; Sr *b* 667.0 ; Sr *c* 658.5 ; Sr *d* 460.8.

BARIUM (IX,10) has a number of fine lines in the orange, yellow and green portion of the spectrum, of which the brightest are, three in the green, Ba *a* at 524.0 ; Ba *b* at 513.0 ; and Ba *d* at 535.0, nearly coincident with the single green line of thallium. Greenish-yellow, Ba *c* at 553.5 ; orange, Ba *e* at 606.2 ; besides several fainter lines and bands in red, orange, yellow and green.

MAGNESIUM (IX, 11) shows a flame spectrum only when the metal is burnt, when a triple green line, corresponding to Fraunhofer b appears at 516.7, 517.2 and 518.3, and a faint blue band near the F line. When magnesium salts are added to an alcoholic solution of *purpurin* (a coloring material derived from madder), to which a solution of ammonia and ammonium chloride had been previously added, peculiar absorption bands appear on each side of the E line in addition to the normal absorption of purpurin (see plate No. 29). They are very similar to those produced in the same solution by *aluminium* salts, but disappear upon addition of acid while those of aluminium remain.

THALLIUM (IX, 12) shows a very brilliant single green line at 534.9, nearly coincident with Ba *c*, and at higher temperature a faint yellow line at 568.0.

INDIUM (IX, 13) in the flame shows a bright indigo line at 451.0. Three other bright lines are produced by the electric spark: a violet at 410.1, a green line at 525.0, and an orange at 619.3.

GALLIUM in the flame shows a feeble violet line at 417.0; another at 403.1 becomes visible by the spark.

LEAD OXIDE, at the temperature of the Bunsen flame, shows a number of lines, of which one orange, at 626.0; one yellow, at 570.0; one greenish, at 548.0, and two green lines at 534.5 and 518.7, are brightest.

COPPER CHLORIDE colors the flame differently, according to the quantity introduced. With a larger quantity the nucleus is orange, with a blue and a green outer envelope; as decomposition proceeds, the nucleus becomes first blue, then green. The spectrum shows many lines at 650.0, 626.0, 603.0, 550.0, 541.0, 534.0, 497.5, 486.5, 481.0, 476.5, 454.0, 450.5, 445.5, 442.8 and 438.0. Of these, three greenish-yellow lines are brightest, while the nucleus is orange. They fade as the nucleus becomes blue, while the other lines gradually appear. When the nucleus of the flame turns green the lines become fainter, while diffuse bands appear.

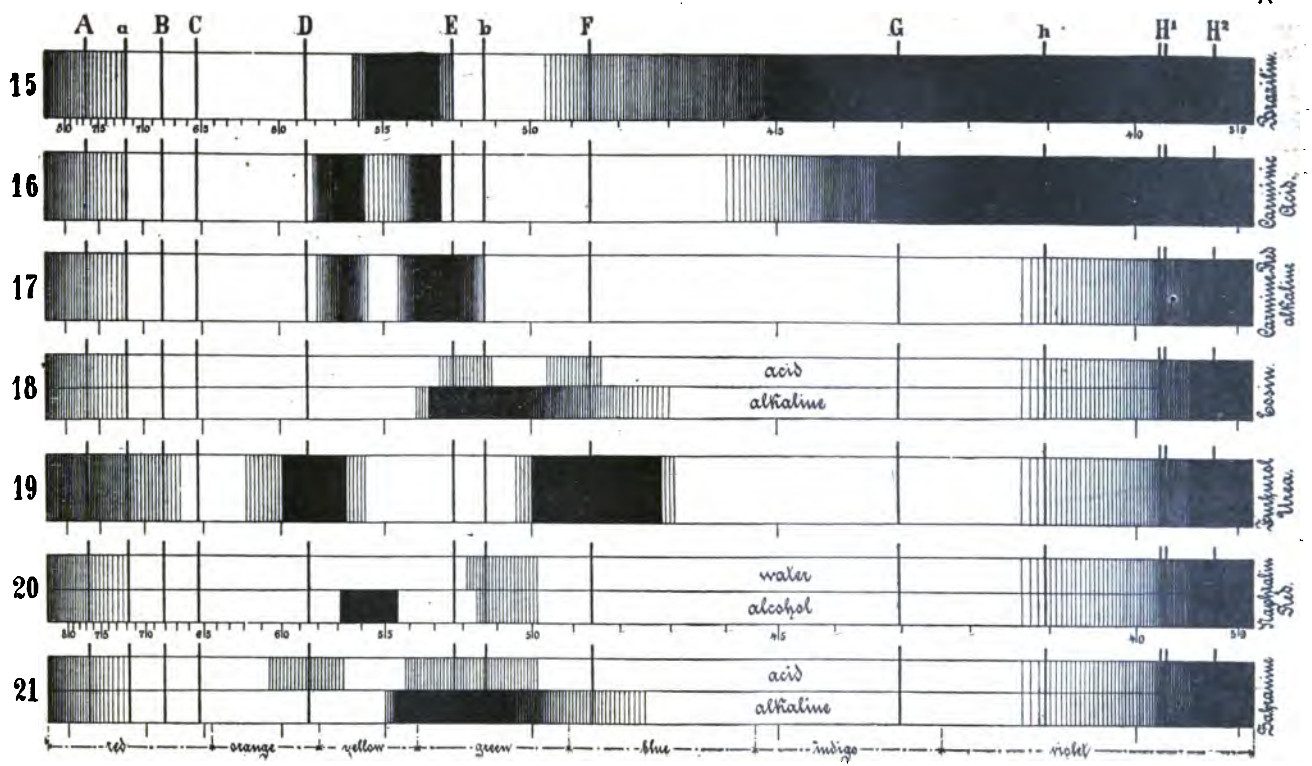
CADMIUM shows a green line at 508.5 and two blue at 479.9 and 467.7.

GOLD CHLORIDE colors the flame green and gives a spectrum of 7 lines at 479.3, 506.3, 523.0, 565.8, 572.7, 583.6 and 627.8.

TIN. Stannous chloride and other volatile tin salts color the tip of the flame red, and the spectrum shows diffuse bands near 645, 580, 560 and 450.

MANGANOUS CHLORIDE shows a flame spectrum of 6 groups near 620, 580, 550, 530, 520 and 500, which, by instruments of higher dispersion, are resolved into many lines. Other compounds of manganese give, at higher temperature (Bessemer converter), many more bright lines in the blue and violet.

CARBON MONOXIDE (VIII, 2) shows diffuse bands in orange, yellow, green, blue and indigo, which coalesce into lines in instruments of low dispersion, but by higher powers are resolved into distinct lines. The brightest lines are in orange from 618.7 to 595.4; in yellow, from 563.3 to 546.6; in green, from 516.4 to 509.8; in blue, from 473.6 to 468.2; in indigo, from 438.1 to 431.1. They are best observed in the lower cooler part of the Bunsen flame, but appear in the flame of all carbon compounds.



A a B C D E b F G h H¹ H²
15 Brazilin.
16 Carminic Acid.
17 Carmine Red alkaline
18 Eosin. acid alkaline
19 Furfurol Urea.
20 Naphtalin Red. water alcohol
21 Safranine acid alkaline
red orange yellow green blue indigo violet
X

dark. A light interval can be distinctly seen between the D line and the margin of the first band, which extends from 578 to 560. The second band reaches from 548 to 520. The difficulty of recognizing the joint spectrum of C O haemoglobin and oxyhaemoglobin in blood only partly saturated with C O may be overcome by reduction of the oxyhaemoglobin by means of yellow ammonium sulphide (or, according to *Jaederholm*, by a mixture of rochelle salt and ammonium-ferrous sulphate), which eliminates the bands of oxhaemoglobin, but not those of C O haemoglobin. Another method of recognizing C O in blood, also proposed by Jaederholm, consists in the conversion into C O haematin. The blood is shaken in a test-tube with twice its volume of 30% sodium hydrate solution. The coagulum, in absence of C O, has a greenish color, gradually turning into red-brown. If C O is present the color is red from the formation of C O haematin. From these coagula a watery solution is made for examination of the spectrum.

C O HAEMATIN (XI, 28) when unmixed shows two bands in nearly the same position as oxyhaemoglobin, but fainter, extending from 589 (D) to 564 and from 545 to 526 (E). When haematin is mixed with it the two bands combine by an interval of lesser shade with a darker stripe near 550.

RED WINE (XII, 30) gives a spectrum greatly resembling that of fresh blood in 1% aqueous solution. The unshaded space of the spectrum extends only from 710 to 620; from thence a half-shade gradually increases in density towards the violet. On diluting the bright space extends more towards D. When made alkaline by addition of ammonia the shade recedes to E, but a dark band forms from 656. (C) to 610. In case of fraudulent coloration by *malva*, the same band extends 656 (C) to 540; when *elderberries* or *whortleberries* are used for coloring the band begins at 635 and extends to 540, where it joins the half-shade, which gradually darkens towards the violet end.

FUCHSIN (XII, 31) has a very dark band reaching from 587 (near D) to 517 (near b); no absorption at the ends other than that by reflection of sunlight. It somewhat resembles the spectrum of haemoglobin.

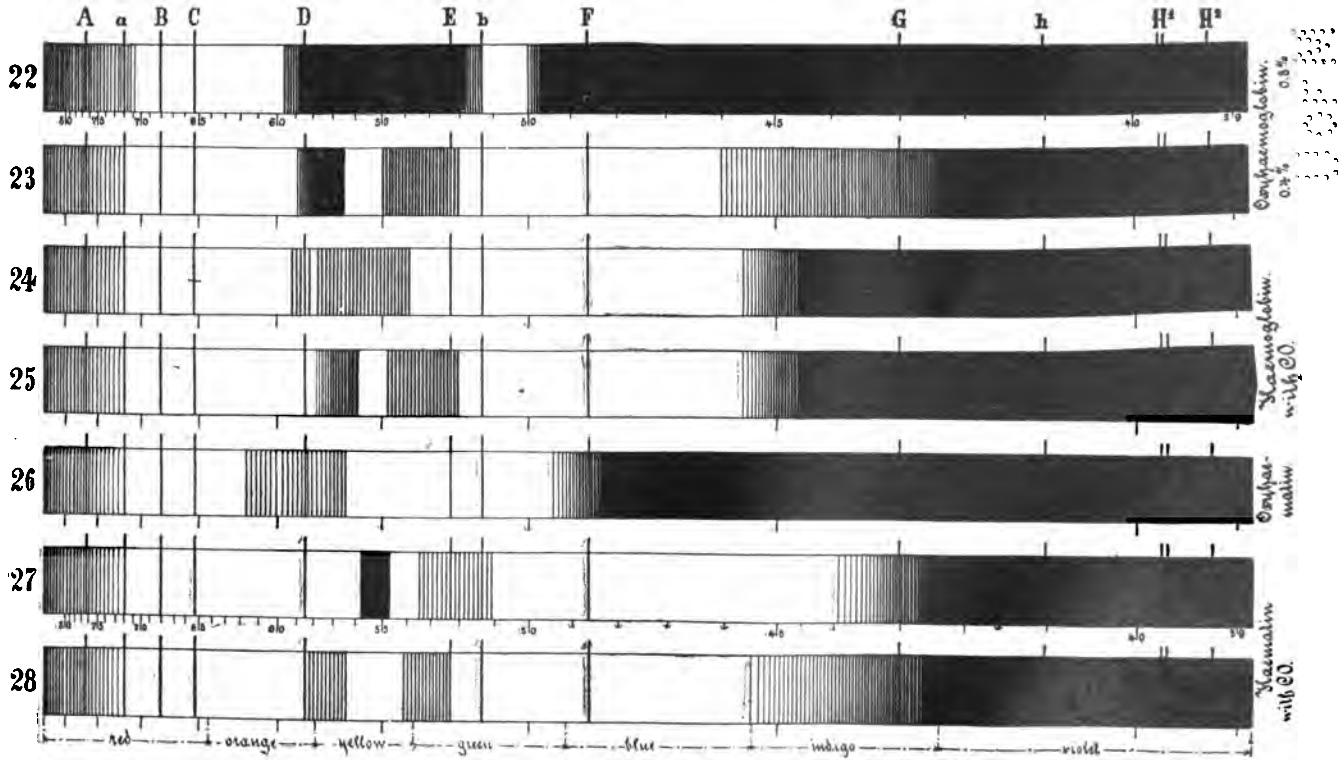
ANILINE BLUE shows a very dark absorption band from 656.2 (C) to 550, gradually shading off from there to 520 (between E and b). *Diphenylamine blue* and some other blues show a nearly identical spectrum. In *mauve violet* in concentrated solution, the dark band begins at 670 and extends to 610, from whence it gradually shades off to 565.

CHLOROPHYLL in alcoholic solution shows a number of dark stripes. Four of these coalesce by intervening half-shades into a band extending from 686.7 (B) to 536. The first, broadest and darkest, from 686.7 to 645, remains visible even in great dilution. The other three are only produced by concentrated solutions. The second lays between 628 and 612, the third between 585 and 575, near the D line; the fourth between 544 and 536. From the F line on a perfect absorption reaches to the violet end. In very dilute solution this resolves into 3 darker bands with intervening half-shades.

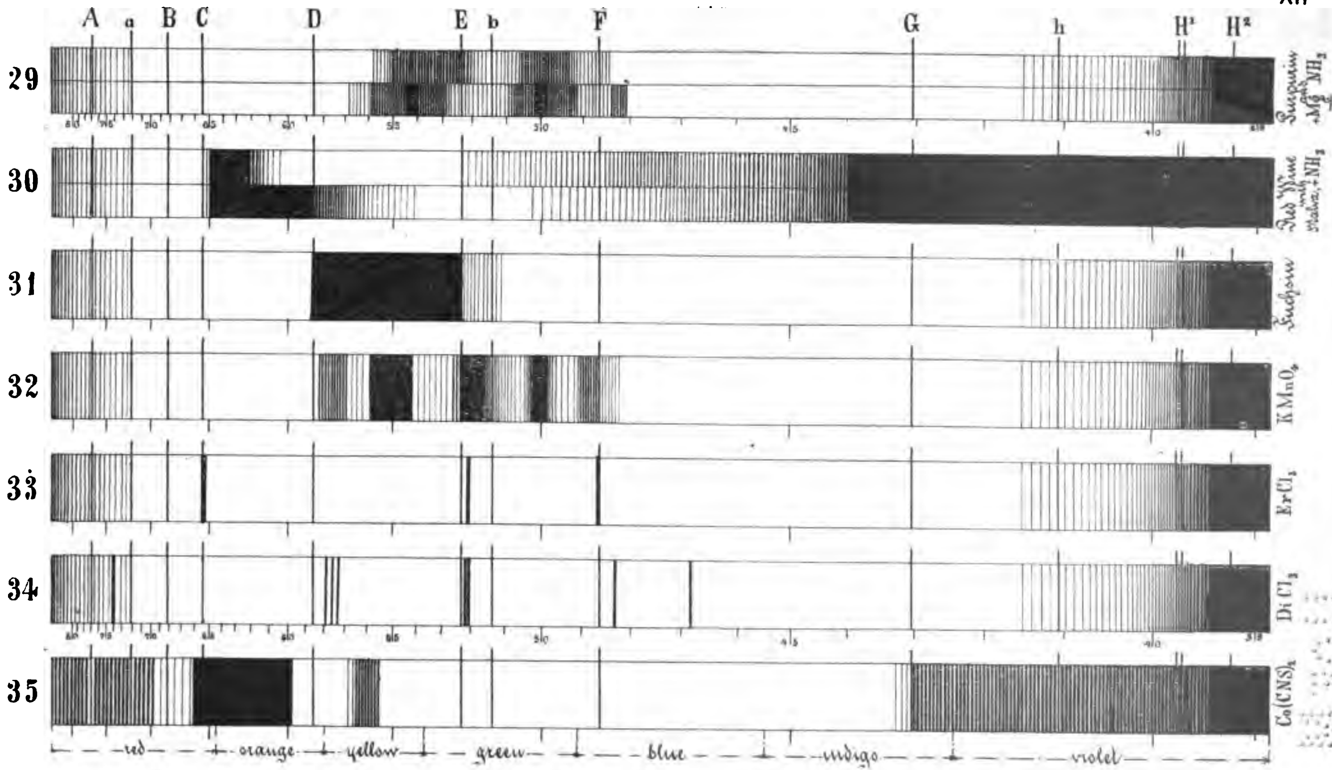
FRAUNHOFER LINES, produced by absorption in the solar atmosphere by various elements, are designated by letters of the alphabet, and have the following wavelengths, expressed in millionths of a millimetre :

A	760.400	Nitrogen.
a	718.360	Nitrogen.
B	686.710	Nitrogen.
C	656.210	Hydrogen *a*.
D 1	589.513	Sodium *a*.
D 2	588.912	Sodium *b*.
D 3	587.500	Helium.
E	526.913	Iron.
b 1	518.310	Nitrogen.
b 2	518.30	Magnesium.
b 3	517.20	Magnesium.
b 4	516.70	Magnesium.
F	486.074	Hydrogen *b*.
G	430.725	Iron.
h	410.120	Hydrogen *d*.
H1	396.810	Hydrogen *e* (Ca, Fe).
H2	393.300	Iron (Ca).

XI


A a B C D E b F G h H¹ H²
22
23
24
25
26
27
28
80 75 70 65 60 55 50 45 40 39
red
orange
yellow
green
blue
indigo
violet
Oxyhaemoglobin. 0.8%
0.4%
Haemoglobin.
Haemoglobin with CO.
Oxyhaematin
Haematin with CO.

XII



A
a
B
C
D
E
b
F
G
h
H¹
H²
29
Purpurin and +Mg +NH_3
30
Red Wine with Malva, +NH_3
31
Fuchsin
32
$KMnO_4$
33
$ErCl_3$
34
$DiCl_3$
35
$Co(CNS)_2$
red
orange
yellow
green
blue
indigo
violet

darker than that of the carminic acid, and extends from 500 to 530, the other from 550 to 570. Addition of alkali moves both toward the red end (see plate X, 17). There is great danger of mistaking carminic acid for haemoglobin (compare XI, 23 with X, 16).

EOSIN (X, 18), see page 79. The red, aqueous solution of the commercial potassium salt fluoresces strongly. Addition of acids destroys this fluorescence, alkalies restore it. The acid solution has two slightly shaded bands, one uniting the lines E and b, the other on both sides of F. Addition of alkali increases the darkness of the first, and the two not only coalesce, but spread from 470 to 530. The ends of the spectrum show no other absorption beyond that occasioned by the reflection of the solar light in which they are observed. The spectrum is easily distinguished from those of blood.

NAPHTHALIN RED (X, 20), also called Magdala red, in alcoholic solution forms a spectrum which might be easily mistaken for that of oxyhaemoglobin. The darkest band reaches from 575 to 545 a, the lighter shaded one from 520 to 500; no other absorption at the ends of the spectrum. The watery solution shows only the dimmer of the two bands from 530 to 500.

SAFRANINE (X, 21), see page 176, in acid solution has two faint absorption bands, coincident with but much broader than those of C O haematin (XI, 28); they reach from 610 to 570 and from 540 to 500. On addition of alkali the first one of the bands disappears, the second darkens and extends considerably towards the more refrangible end, from 550 to 475. No absorption at the ends beyond that by reflection of the sunlight.

FURFUROL-UREA (X, 19). The purple solution resulting from the mixture of furfurol, urea and hydrochloric acid, shows two broad and dark absorption bands, one from 600 to 565, another from 500 to 471, both with lighter shades added to each side; the red end of the spectrum is shaded up to 670. (See on page 105.)

BLOOD may be recognized readily by the absorption spectra of its coloring matters and their modifications by absorption of gases.

Haemoglobin (cruorin) readily absorbs the atmospheric oxygen and becomes *oxyhaemoglobin*, or may be oxidized by permanganate, etc., to *methaemoglobin*. Heating, especially with acids or alkalies, converts haemoglobin into *haematin*, whose hydrochlorate is known as *haemin*. All of these give characteristic spectra.

OXYHAEMOGLOBIN in concentrated solution (or fresh, normal blood) is impervious to light in tubes of 1 Cm. diameter. As

the solution is diluted to 1% it shows a narrow strip of red, which with greater dilution expands, and when the solution contains 0.8% shows the spectrum No. 22, having a dark band from D to half way between E and b, with a lighter shade added to each end, so as to reach from 597 to 513, while the violet end of the spectrum is entirely obscured from 500 to the end. Greater dilution (see No. 23) makes this shade lighten and recede to 460, while the broad central band separates into a narrow dark band from 590 to 567, and a fainter one from 550 to 520. With still greater dilution these bands become narrower, and finally, in a 0.01% solution, only the darker one remains from 582 to 575. When the solution of oxyhaemoglobin is gently heated with a little weak solution of alkaline hydrate, the bands coalesce and move toward the red end, forming the spectrum of

OXYHAEMATIN (XI, 26), characterized in dilute solution by a single band extending from 625 to 505. Greater concentration enlarges this band at both ends until the interval between it and the absorption from the violet end becomes shaded.

When oxyhaematin is boiled with more concentrated alkaline hydrate, it is converted into *reduced*

HAEMATIN (XI, 27), whose spectrum has 2 bands, a very dark one from 558 to 548, and a fainter one from 535 to 511; the shading of the violet end reaches only to 439. The addition of a little alcohol and oxalic acid in slight excess changes this spectrum to 4 bands, one between C and D, one a little beyond D, a third broader one near E, and the broadest, fourth, near the F line.

SULPHOHAEMOGLOBIN. When pure, this has a narrow absorption band at 620, which is super-added to the spectrum of haemoglobin, when this has not been entirely converted. It is produced by saturating blood with hydrogen sulphide or by reducing oxyhaemoglobin by yellow ammonium sulphide, when the oxyhaemoglobin bands disappear, while those of C O haemoglobin remain unaffected.

HAEMOGLOBIN, HAEMATOCRYSTALLIN or CRUORIN (XI, 24), as contained in blood after removal of the oxygen, shows violet and green dichroism. In dilution of 2% it shows a dark band from 595 to 535, with a lighter interval near 575. It also absorbs the violet from 408 to the end. After saturation with carbon monoxide, blood contains no more oxyhaemoglobin, but, instead of it,

C O HAEMOGLOBIN, whose spectrum, to the careless observer, shows little difference from that of oxyhaemoglobin, but in reality has its bands further removed from the red end and slightly less

LIST OF TESTS.

Arranged under the names of the substances to which they are applied.

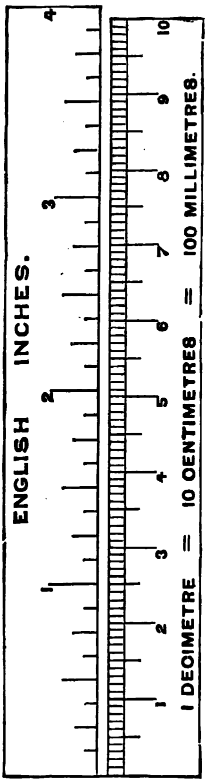
RELATIONS OF METRIC TO U. S. MEASURES AND WEIGHTS.

The metric *unit of length* is obtained by dividing the distance from the earth's equator to the pole into 10,000,000 parts. It is called the **Metre** and corresponds to 30.37079 English inches, according to the standard of conversion authorized by the U. S. Congress and by the British Parliament. (Clarke's correction, 1 metre = 39.370432 inches, has been adopted by the U. S. Pharmacopœia.)

It is subdivided and multiplied, as follows:

1 Metre = 10 **deci**metres = 100 **centi**metres = 1000 **milli** metres.

1000 metres = 1 **kilo**metre = 10 **hekto**metres = 100 **deka**metres.



1 inch = 25.3995 millimetres.

1 foot = 304.794 millimetres.

1 **cubic decimetre** is the *unit of volume*, called the **litre**, and equals 1000**cubic centimetres** (Cc.) or **milli**litres.

1 litre = 33.81 fluid ounces = 2.1135 pints = 0.26419 gallons, wine measure (= 1.76 pints imperial measure).

1 millilitre = 1 cubic centimetre = 16.23 minims.

1 minim = 0.06 Cc.; 1 fluid ounce = 29.58 Cc.; 1 pint = 473.148 Cc.; 1 gallon (wine measure) = 3785.15 Cc.

The *unit of weight* is called the **gramme** (gr.). It is the weight of 1 cubic centimetre of water at 4° C., its point of greatest density.

The gramme is subdivided and multiplied, as follows:

1 **gramme** = 10 **deci**grammes = 100 **centi**grammes = 1000 milligrammes.

1000 grammes = 1 **kilo**gramme = 10 **hekto**grammes = 100 **deka**grammes.

1 Cc. water weighs 1 gr.; 1 litre water weighs 1 kilogr.

1 gramme = 15.43234874 grains troy.

1 kilogramme = 2.6803 pounds troy = 2.20462 pounds avoirdupois.

1 grain troy = 64.799 milligrammes.

1 pound avoirdupois = 453.6 grammes.

1 gramme per litre = 58.329 grains troy per wine gallon (= 70 grains troy per imperial gallon).

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